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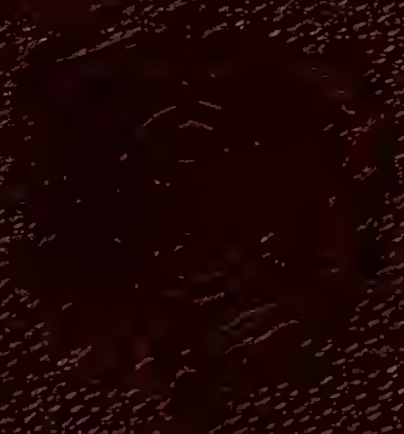

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QUANTITATIVE INORGANIC ANALYSIS

WITH SPECIAL REFERENCE TO THE ANALYSIS OF
CLAYS, SILICATES, AND RELATED MINERALS:

BEING

VOL. I. OF A TREATISE ON THE
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Dedicated to my Friend
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PREFACE.

This book is to be considered as the first volume of a treatise on the Ceramic and Silicate Industries. The part dealing with clays and related materials was expanded from a special course of lectures I gave on that subject about three or four years ago; but, as the work developed, it was thought best to collect all the analytical operations into one volume and thus avoid abrupt changes of subject in the more technical parts, to be published later, and sometimes referred to as "Volume II."

The processes here described are those at present used in the Testing Department of the County Pottery Laboratory, Staffordshire, for the analysis of clays, bricks, and related materials; for glazes and enamels; for colouring mixtures; for the special refractories introduced in recent years; etc. The book is divided into five parts. Some general analytical processes are described in Part I.; the analysis of a typical simple silicate is discussed in Part II.; the methods to be adopted with more complex silicates—glazes, enamels, colours, etc.—are indicated in Part III.; while Part IV. shows the modifications required when some of the more difficult, as well as some of the rarer, elements are present. The last part—Part V.—indicates methods to be employed when acidic elements have to be determined, and a chapter on the so-called "rational analysis" concludes the volume. Some useful reference tables are included in an Appendix. The methods of testing clays and clay products, as distinct from analysis proper, will be described in Vol. II.

The method for the analysis of a typical silicate detailed in Part II. of this book is perhaps that which gives the most accurate results—so far as our present knowledge goes—for clays, silicate rocks, silicate minerals, and related materials. The work of W. F. Hillebrand of the U.S. Geological Survey has been largely instrumental in developing this branch of analysis to its present condition. These methods do not allow analyses to be conducted with that speed required in certain industrial work, and accordingly I have indicated the short-cuts available to those who have mastered the general methods. So many handbooks have been published which specialise in cement, water, and fuel analyses that these subjects have not been elaborated particularly here.

Many of the analytical processes have been described on typed sheets for six or seven years, and employed by the students of the analysis class of the Pottery School, and by the professional staff in the Testing Department. The questions which have been asked from time to time have enabled me to strengthen many weak places in the descriptions of the methods. Early proofs have also been used in the laboratory for over a year, and the descriptions of the more common analyses must have been verified at the bench by a score of different workers. During this time, the great mass of literature on the subject has been overhauled anew, and the extensive footnotes indicate where papers bearing on the subjects discussed in the text can be found. The reader must thank the publishers for giving me every facility for elaborating the original proofs after their handling in the laboratory. I am specially indebted to my colleagues Messrs A. D. Holdcroft, J. C. Green, and C. Edwards for the trouble they have taken in reading the proofs; to Miss M. Chetham for help with the indexing; and to Mr F. J. Austin for photographing the apparatus and specimens.

J. W. M.

County Pottery Laboratory,
Stoke-on-Trent.

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INTRODUCTION.

The Subdivisions of Analytical Chemistry.

Qualitative and Quantitative Analysis. — The general purpose of analytical chemistry is to find the chemical nature of a given material. With simple substances this is comparatively easy, for the object of the analysis is easily secured by establishing the identity of the given substance with one whose properties are known. A simple inspection of the consistency, colour, or smell may suffice; in other cases, the specific gravity, boiling point, or freezing point may have to be determined; and finally, it may be necessary to prepare compounds of the given substance, and compare their properties with those of known compounds. Thus arise the so-called *tests* of qualitative analysis. On the other hand, if the substance to be analysed be not simple, but is rather a complex mixture of several simple substances, the analytical operations are more intricate, for the properties of the different components in the complex may be masked by the mere presence of the others so as to render identification impossible. In that case, the complex must be resolved into simpler substances which can be separately identified.

If the purpose of the analysis be merely identification, the operations are said to be *qualitative*; while if the amount of one or more of the constituents has to be determined, the analysis becomes *quantitative*. There is a large number of manuals on qualitative analysis in which an elaborate general scheme —over fifty years old—is described for the identification of the constituents of the most complex inorganic mixtures. In many cases, this scheme is only of pedagogic interest, because, in practice, we generally possess a good idea of the components of a mixture, and only the amounts of the more important of these are industrially important. Hence, although a qualitative analysis should precede the quantitative, yet numerous quantitative analyses are made without the preliminary examination, because the qualitative composition of the given substance is well enough known.

Gravimetric Analysis.—In the gravimetric analysis, the several constituents are separated and weighed, or, if they cannot be separated, or if they are unsuited for weighing, they are converted into compounds of known composition which can be satisfactorily weighed. The several steps in the operation are:

(1) A definite amount of the substance to be analysed is weighed.

(2) The weighed sample is brought into solution.

(3) The constituents to be determined are separated from the solution, one by one, in the form of definite insoluble compounds, either by precipitation or by electrolysis—*electro-analysis.*

(4) A compound so separated is freed from adherent liquids and solids by filtration and washing.

(5) The compound is dried and ignited so as to convert it into a stable pure compound.

(6) The compound is weighed.

(7) The amount of the substance to be determined is computed by known arithmetical processes from the weight of the ignited compound.

Volumetric Analysis.—In volumetric analysis, the quantity of a constituent in a given solution is determined by adding a sufficient volume of a *standard* *solution*—containing a known amount of a selected reagent—to produce a definite "complete" reaction. The number of operations involved in a gravimetric analysis is here much curtailed; as a rule, no filtration or washing is needed; nor is any weighing required after the sample has been brought into solution. The operations are:

(1) A definite quantity of the substance to be analysed is weighed.
(2) The weighed sample is brought into solution.
(3) The standard solution of the selected reagent is added until the whole of the substance to be determined has been converted into a definite compound. The completion of the reaction is indicated by a change in the colour of the solution, frequently tinted with a selected dye called the *indicator*.
(4) The quantity of the standard solution required to complete the reaction enables the amount of the substance under investigation to be computed by known arithmetical processes.

Gasometric Methods of Analysis.—If the substance being analysed gives off a gas when it is treated with a selected reagent, such that the volume of gas liberated bears a definite relation to the amount of the constituent in question, the measurement of the volume of the liberated gas, or a determination of the loss of weight which occurs when the gas is all expelled, enables the amount of the constituent to be computed by arithmetic.

Physical Methods of Analysis.—There are several so-called physical methods of analysis in which the variation of some property—say, specific gravity—is proportional to the amount of the substance under investigation which is present in a given mixture. A determination of that property enables the amount of substance to be computed. In *colorimetry*, for instance, the substance under investigation can be made to produce a coloured solution such that the intensity of the colour varies with the concentration. A comparison of the tint of a known volume of the solution with that of another solution containing a known quantity of the same substance as that under investigation, enables the amount of the given constituent to be computed by simple arithmetic. In *turbidimetry*, instead of comparing the colours, the degree of opacity of the two solutions is compared. This process is of limited application, and is only possible when the solution under investigation can furnish a fine-grained solid precipitate which settles very slowly.

The Birth of Analytical Chemistry.

The chemists of the phlogiston period — Basil Valentine, O. Tachenius, F. Hoffmann, A. S. Marggraf, C. W. Scheele, etc.[1]—made a large number of isolated observations which enabled many inorganic substances to be distinguished from one another. Robert Boyle,[2] about 1661, styled the process of identification an *analysis*. About a century later, Bergmann[3] compiled and arranged the different tests in a systematic and methodical way, and thus laid a foundation upon which Berzelius and Rose[4] built a system of qualitative analysis which has persisted with remarkably few changes up to the present day.

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[1] B. Valentine, *Chymische Schriften*, Leipzig, 1769; O. Tachenius, *Hippocrates Chemicus, qui novissimi salis antiquissima fundamenta ostendit*, Venetiis, 1666 (English trans., London, 1677); F. Hoffmann, *De Methodo Examinandi Aquas Salubres*, Leyden, 1708; A. S. Marggraf, *Chymische Schriften*, Berlin, 1761–7—"Method of reducing silver chloride without loss," 1749; "Chemical examination of water," 1754; C. W. Scheele, *Opuscula chemica et physica*, Lipsiæ, 1788–9.

[2] R. Boyle, *The Sceptical Chymist*, Oxford, 1661; *Experiments and Observations upon Colours*, London, 1663.

[3] T. Bergmann, *Opuscula Physica et Chemica* (*De minerarum docimasiâ humidâ*), Holmiæ, 1780.

[4] J. J. Berzelius, *De l'Analyse des Corps Inorganiques*, Paris, 1827; H. Rose, *Handbuch der analytischen Chemie*, Berlin, 1829.

The earliest writings on metallurgy show that from remote antiquity metals have been extracted by heating their ores with appropriate fluxes ; and there can be little doubt that laboratory methods for the dry or fire assay [1] of ores were modelled upon metallurgical operations conducted upon a large scale. Witness the so-called Cornish process for the assay of copper [2] is conducted very much the same as that which has been employed for the extraction of copper from its ores for thousands of years ; and the origin of the method of separating silver from lead by cupellation cannot be traced, because it is alluded to by early writers [3]—Diodorus, Strabo, Suetonius, Pliny, etc.—as an old and familiar process.

Bergmann's Work.—T. Bergmann's brochure upon "the analysis of minerals in the wet way" was published in 1780. In this important essay, Bergmann pointed out the existence of errors in dry or fire assaying processes due to the incomplete attack of the minerals by the fluxes ; to the retention of some of the metal by the slag; etc., and he advocated several wet processes in preference to the dry methods of analysis then in vogue.[4] Bergmann [5] also showed that the amount of a substance in solution was best determined by converting it into a definite compound of known composition, and subsequently deducing the amount of the desired constituent from the weight of the compound so prepared.[6] Thus lime was weighed as oxalate or sulphate ; lead, as sulphate or sulphide ; sulphuric acid, as barium sulphate ; silver, as chloride, etc., although, previous to this, Marggraf [7] had determined the amount of silver in alloys by separating the silver as an insoluble chloride. Bergmann recognised that "the sum of the weights of each of the constituents in an analysis should be equal to the weight of the mineral analysed, allowing for a certain loss during the manipulations," and his analysis of a sample of pure gypsum is singularly good, *e.g.* :

	Vitriolic acid.	Calcareous earth.	Water.
Bergmann's analysis .	46	32	22 per cent.
	Sulphur trioxide, SO_3.	Lime, CaO.	Water, H_2O.
Modern analysis . .	46·5	32·5	21·0 per cent.

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[1] The term *assaying* is applied more or less vaguely to methods of chemical analysis which are confined to the determination of the commercially important constituents in given materials. Thus, processes for the assay of vegetable products, drugs, ores, alloys, etc., are described in current literature. The assay of ores, alloys, and related products can be conducted by treating the material under investigation with suitable solvents so as to get the desired metal in a solution from which it can be subsequently precipitated—*wet or solution processes* ; or the given material may be fused with a suitable flux so that the desired substance is reduced to the corresponding metal, which collects as a button at the bottom of the crucible, and the associated substances can be separated in the form of a fusible slag—*dry or fire processes*.

[2] M. L. Moissenet, *Ann. Mines* (5), **13**. 183, 1858.

[3] Thus, in the second century B.C., Agatharchidas of Cnidos described the method employed by the Egyptians for purifying gold, and this resembles the cupellation process for separating silver and lead. C. S. Pliny, *Naturalis Historiæ*, Venetiis, **33**. 44, 1472 ; **34**. 48, 1472 ; G. Agricola, *De Re Metallica*, Basiliæ, 1546 (English trans., London, 1913) ; A. Libavius, *Ars probandi Mineralia*, Francofurti, 1597 ; A. Libavius, *De Judicio Aquarum Mineralium*, Francofurti, 1597. The two last-named essays are usually stated to be the first books specially devoted to the analysis of minerals. The first-named is considered to be largely compiled from Agricola's book. See also G. Chesneau, *Revue Scientifique* (5), **3**. 321, 357, 1905.

[4] A. P. T. Paracelsus (*Opera Omnia Medico-Chemico-Chirurgica*, Geneva, 1658) is generally credited with having first described an analysis in the wet way. To analyse an alloy of gold and silver, Paracelsus treated the sample with nitric acid—*aqua fortis*—which dissolves the silver and leaves the gold behind in the form of an insoluble black powder. He then precipitated the silver by inserting a plate of copper in the solution. The copper is at the same time vigorously attacked by the free acid.

[5] T. Bergmann, *Opuscula Physica et Chemica* (*De minerarum docimasiâ humidâ*), Holmiæ, 349, 399, 1780.

[6] In 1755, J. Black (*Experiments on Magnesia alba, Quick-lime, and other Alcaline Substances*, Edinburgh, 1777) estimated the amount of magnesia alba in a solution by the addition of sodium carbonate and weighing the resulting precipitate.

[7] A. S. Marggraf, *Mem. Akad. Wiss. Berlin*, 16, 1749.

Bergmann also introduced the method of decomposing silicates by fusion with alkaline carbonates, and his little treatise, *De minerarum docimasiâ humidâ*, is thus considered to have inaugurated a new era in analytical practice.

Klaproth's and Vauquelin's Work.—The next advances were made by Klaproth[1] and by Vauquelin.[2] These workers introduced many improvements in *technique* and analysed many minerals. Klaproth, for instance, ignited his precipitates before they were weighed in cases where the ignition was not attended by decomposition. Quantitative analysis was greatly stimulated by the need for separating the different constituents of the minerals from one another, during the many investigations on the composition of minerals made about that time. As Klaproth expressed it: "Nature, inexhaustible in her riches, has intended to keep in activity the ardour of the naturalist in the examination of mineral substances." As early as 1808, we can recognise the beginnings of the present-day method of conducting silicate analyses in John's book,[3] which summarised the labours of Bergmann, Marggraf, Klaproth, and Vauquelin.

Berzelius' Work.—About 1827, Berzelius[4] took up the work, and considerably advanced the art by devising a number of new methods for the determination and separation of many elements, and testing those then in use; Berzelius also introduced a number of improved methods in manipulation: *e.g.*, the hydrofluoric acid process for decomposing silicates; the separation of precipitates by filtration through "filter paper," followed by subsequent ignition; and, by using small quantities of the material to be analysed, he reduced the errors of manipulation, because small precipitates are more readily cleaned than large ones. Berzelius' pupils, F. Wöhler and H. Rose, worked up the experience of their teacher with their own in two books: H. Rose's *Handbuch der analytischen Chemie*, Berlin, 1829, and F. Wöhler's *Praktische Uebungen in der chemischen Analyse*, Göttingen, 1853. The later editions of these books are consulted even to-day. About this time also appeared the first edition of Fresenius' famous book (1846), and this was followed by the founding of the *Zeitschrift für analytischen Chemie* in 1862. Thus the modern practice of the art is linked with that of its founders.

Some Uses of Analytical Chemistry.

The information which the analysis is expected to furnish, as indicated on pages 242–3, determines the method by which it is to be conducted. The information required may be purely of scientific interest, or it may be essentially practical. The utility of analyses for purely scientific purposes need not be here scrutinised. It would be easy to quote many examples where analysis has thrown a new light on the aspect of chemistry.[5] Analysis is an indispensable auxiliary to the mineralogist, for, as C. R. Fresenius (1875) has said, it teaches him the true nature of minerals, and suggests to him principles and rules for their recognition and classification. H. S. Washington (1903),[6] too, says that analyses are no longer ornamental adjuncts, but essential parts of most petrological publications, on which most of the discussion hangs, and from which the most important conclusions are drawn.

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[1] M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Freiberg, 1795.

[2] L. N. Vauquelin, *Scherer's Journ.*, 3. 410, 1799.

[3] J. F. John, *Chemische Laboratorium*, Berlin, 181, 1808.

[4] J. J. Berzelius, *De l'Analyse des Corps Inorganiques*, Paris, 1827.

[5] The work of C. F. Wenzel (1777) and of J. B. Richter (1791–1802) on chemical equivalents; the work of H. Cavendish (1784) on the composition of water; of C. W. Scheele (1779) on the composition of air; and the 1800–1808 controversy between C. H. Berthollet and J. L. Proust on chemical combination, illustrate the debt chemical theory owes to analytical practice.

[6] C. R. Fresenius, *Quantitative Chemical Analysis*, London, 1. 4, 1876; H. S. Washington, *Prof. Paper U.S. Geol. Sur.*, 14. 13, 1903.

In industrial work, the purpose is essentially utilitarian, for the analysis is generally directed to finding the composition of commercial materials, and to answering such questions as: (1) Does the material to be purchased correspond with the seller's description? (2) Is the material suitable for the purpose for which it is required? (3) Is the material really worth the quoted price?

The Real Value of Rough Working Tests.—The practical potter usually tries how a small sample of the material to be purchased behaves in his oven, and if it satisfies that test, he accepts the bulk, believing with blind faith that all is right. It does not need the *subtilis diabolus*, referred to on page 127, to deceive him, for, when it is worth while, it is comparatively easy to devise adulterations for most potter's materials which will make satisfactory trials. Although this simple test, invaluable in its way, may show (1) whether or not any *deleterious* impurity is present, or (2) whether the material is or is not capable of doing the work for which it is intended; yet (*a*) it gives no information as to the presence or absence of inert admixtures; otherwise expressed, it does not say whether the material offered for purchase really corresponds with the seller's description; and (*b*) it gives no idea whether the material is really worth the price asked.

Impurities in the Raw Materials.—An intimation to the vendor that the material may be tested is not sufficient security for the buyer. I am told that "of the samples of materials offered to a Government Department, approximately forty per cent. are either adulterated or of very inferior quality." Price is no criterion of the quality, for it is said that the most inferior samples were sometimes quoted at the highest prices. In such cases, analyses and tests are the purchaser's only safeguard, and the cost of the analysis in large deals may be recompensed a thousandfold.

Four samples of tin oxide from four different firms were submitted for analysis. The chemist reported that three of the samples were very nearly the same, and contained approximately 99·5 per cent. of stannic oxide, but the fourth sample contained 5 per cent. of "combined water," and $\frac{1}{20}$th per cent. of tungstic oxide as impurity. The potter's trials, however, showed that the cheapest and least pure sample gave the richest opaque glaze! The first three samples were approximately £228 per ton, and the fourth sample £222 per ton. The potter subsequently obtained a rebate on account of the 5 per cent. of combined water, and the fact that the effective tin oxide in the sample A cost £229·15 per ton, and in the sample B, £240 per ton; and learned incidentally that he might be able to do with rather less stannic oxide than he had previously employed when tin oxide was not so expensive.

The Adulteration of Raw Materials.—So long as human nature is what it is, so long will adulteration be carried on with a view of making large profits, and of cheating the purchaser into paying too high a price for his materials. *Caveat emptor*—let the buyer beware. A glance through the records of any testing laboratory shows that successful adulteration is one of the fine arts. Certificates of analysis of samples selected by the vendor are commonly presented as if some mysterious virtue resided in a material with such a certificate appended. The sample placed in the analyst's hands may or may not represent the material sold by the dealer. The onus of proof that the certificate really represents the materials received by the purchaser, rests with the vendor (see page 127). The preceding example—tin oxide—was not a case of deliberate adulteration. The next case is not so clear.

A traveller offered a sample, A, of white lead at £28 per ton (5 per cent moisture), another traveller offered another sample, B, at £25 per ton (5 per cent. moisture). The cheaper sample gave the better-looking frit when fused with a given proportion of ground flint in a biscuit cup in the usual way. Analysis showed that the cheaper sample B contained 69·0 per cent. of PbO, and 15 per cent. of barium carbonate, whereas the dearer sample A contained 81·6 per cent. of PbO, and no barium carbonate. Ground witherite (94–96 per cent. barium carbonate) is worth about £10 per ton. The effective PbO in sample A would cost £34·31 per ton, and in sample B, £36·23 per ton. Hence, the dearer sample is the cheaper. The improved colour of the frit from the cheaper sample B was due to a known secondary effect of the barium salt which is of no significance when the material is used in bulk.

Standardising the Products of a Factory.—Analysis also furnishes a valuable means of keeping the finished products of a factory up to standard. Suppose that the body and glaze be analysed when everything is at its best, and the results be kept as standards. The standards are then very convenient for reference when substituting fresh clays or other raw materials, in order that the type of the new body may be kept as nearly as possible like the old one, so as to lessen the risk of complications with the glaze, etc. In many cases, too, the cause of those perplexing faults which sometimes crop out, and which are usually attributed to the miller or to wrong mixtures, can be unerringly located and promptly rectified by a comparison of the analysis of the defective body or glaze with the standard.

A fresh batch of glaze turned out highly unsatisfactory. The glaze-mixer affirmed that he had mixed the glaze precisely as he had always done before, and it was found that the defective glaze had received no different treatment from that regularly employed on the works. The miller was accordingly blamed for the fault. He sent a sample of the defective glaze along with a sample of good glaze from the previous mixing for analysis. The analyst reported that the good glaze contained the equivalent of 24·5 per cent. of lead oxide, PbO, and the bad glaze but 5·5 per cent. The proportions of the other constituents were the same in both glazes. The fault was obviously due to a wrong mixing, in spite of affirmations to the contrary. When the proper proportion of white lead, computed from the analysis, was added to the defective glaze, it proved quite satisfactory.

The Imitation of Commercial Products.—In the *Sturm und Drang* of commercial warfare, it is not only necessary for a firm to test its own materials and products, but the "Intelligence Department" must also keep a watchful eye on the products of rival manufacturers.

A manufacturer has for years been supplying the trade with, say, an opaque glaze made from an old recipe—a legacy from the founder of the firm. For perhaps half a century there has been no change in quality for better or for worse, and the old recipe is the real master of the works. The traveller reports that he is seriously menaced by the success of a foreign glaze which is considerably better than his own and quite as cheap. Faith in the long-cherished recipe is shattered. After much worry and expense, trial and failure, the manufacturer is inclined to give up ignominiously beaten. As a last resource, he sends a sample of the foreign glaze to the expert analyst, requesting a recipe. The chemist recognises that it is not much use trying to reproduce the unknown glaze until he knows its composition. Guided by the analysis, it is comparatively easy to make a successful imitation of the competing glaze. There is no groping in the dark; success is not accidental and fortuitous, but the logical result of methodical work.

This may seem rather a low estimate of the function of an analyst, because a properly equipped staff would not be satisfied with its own old recipes. There would be no standing still. A firm would not wait until its position on the market was jeopardised or made untenable by a rival, but it would be continually experimenting, not directly to imitate its competitors, but rather to beat its own products year by year.

Some Limitations of Analytical Chemistry.

How to Treat the Analyst.—Some have an extraordinary notion of the resources of analytical chemistry, and inquiries are made for all manner of impossible things. A bottle containing about 100 c.c. of water was sent for analysis, and the contents smelt strongly of a patent medicine! The subject of sampling is so important that a special chapter has been devoted to it—pages 127 to 140. When sending materials to the analyst, some consider it best to keep back information concerning the nature and origin of the sample so as to prevent a biassed report. The general effect of this procedure is to render the analyst's task more difficult and costly, and to hamper his usefulness. Owing to the need for completing the analysis in a reasonable time, and at a specified fee, an exhaustive search for every improbable constituent is seldom made. An analyst working under normal conditions would certainly be excused if a clay with an abnormal amount of lithia were reported with soda in place of the lithia.[1] An example is indicated on page 141. This recalls the fact that the presence of arsenic in beer was not suspected until the 1900 epidemic of arsenical poisoning. Consequently, if the amount of any unusual constituent is desired, this should be specified.

The Fallibility of the Analyst.—Perhaps something of the feeling of awe and wonder which prevailed in the minds of the vulgar towards the alchemists of old, survives to-day in the popular concept of the analytical chemist. Many apparently take it for granted that he is gifted with keener and more occult powers than his fellows. As a matter of fact, no one should be more conscious of his own limitations than the analyst himself, for he is continually humiliated and shamed by the fallibility of his own tests, and by the resulting instability of his opinions. Analyses have been published which emphasise in a remarkable manner how men exceptionally expert in one field of analysis fail ludicrously in an unfamiliar field. Not very long ago, a report on china clay by an excellent county analyst "went the rounds." The report had a highly improbable number for the amount of alkali in the clay, and stated that the alkalies were rather low, but the defect could be remedied by the addition of soda! In some cases, it is difficult to believe that the "reputed" analyses have been obtained other than by a process of guessing.

Not infrequently a manufacturer has sent out samples to different chemists, and had different results returned. He may have asked for explanations, and decided in future to avoid the chemists as much as possible, concluding, as one expressed it, that "chemists are bluffers." Unless two chemists are able to analyse the same sample with results acceptable to both buyer and seller, it is difficult to see what other conclusion the commercial man can draw. The utility of analyses in some of the industries has been discredited by ignorant, slovenly work which would be ludicrous were it not so pathetic. Faulty analyses have been discussed in several parts of this book[2]—*e.g.*, pages 222, 248, 365, 610, and 674. What H. S. Washington (1903)[1] has said of rock analyses in general applies even more emphatically to some published work on clays:

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[1] In this connection it is interesting to note that C. F. Plattner (*Pogg. Ann.*, 69. 443, 1846) was not able to make his analysis of the mineral pollux (from Elba) add up to 100 per cent., and he sought in vain for the missing element. After R. Bunsen and G. Kirchhoff (1860) had discovered cæsium, F. Pisiani (*Compt. Rend.*, 58. 714, 1864) showed that Plattner had mistaken cæsium (atomic weight 132·8) for potassium (atomic weight 39·1). By making the corresponding correction, Plattner's analysis was found to be quite satisfactory. To make this quite clear, assume that 5 grams of a compound, supposed to be potassium chloride, are obtained. This will be multiplied by 0·631 to get the equivalent amount, 3·16 grams of K_2O; but if the compound be CsCl, not KCl, then the weight must be multiplied by 0·835 to get the corresponding amount, 4·18 grams of Cs_2O. The analysis would thus appear to be 4·18 less 3·16, that is 1·02 grams too low if the 5 grams of cæsium chloride were mistaken for potassium chloride. This is a remarkable tribute to the accuracy of Plattner's analysis (J. W. Mellor, *Modern Inorganic Chemistry*, London, 356, 1912). Lithium has a smaller atomic weight than sodium, and accordingly, if much lithium is assumed to be sodium, the analysis will total too high.

[2] A recent discussion on the presence of titanic oxide in fireclays can be cited as an illustration of the value to be attached to some brick analyses even by some who say they have analysed "hundreds of bricks," but who have apparently not troubled to find what methods are used by those who have specialised in producing accurate results.—A. R. Myhill, *Gas World*, 58. 299, 364, 1913; F. Harvey, *ib.*, 58. 323, 433, 1913; K. C. Orr, 58. 365, 1913; Anon., *ib.*, 58. 402, 1913.

> There is a tendency to place implicit confidence in the results of analytical work—to accept readily whatever figures the analyst may furnish, with scarcely ever an attempt at a critical estimate of the worth of the analysis. It seems to be taken for granted that the analyst, like the proverbial king, can do no wrong. This applies not to the personal good faith of the analyst, but to the analytical processes which, possibly because they belong to one of the exact sciences, are for the most part tacitly assumed to be infallible. In few cases does there seem to be any recognition of the difficulties and uncertainties of analytical work.

The Fallibility of the Analysis.—Analytical operations are not performed with an automatic instrument which gives the composition of a substance with machine-like precision. The presence or absence of each constituent has to be established by special tests, and the amount determined by a number of operations each of which introduces a small error into the final result. The limits of error in the more frequently conducted operations are fairly well known, and to those familiar with that type of work, the precautions needed to reduce the errors to a minimum are a part of their routine practice. With those substances which are not analysed so frequently, the errors are probably somewhat greater, for the disturbing factors are not so well known. At best, however, few analytical operations are altogether free from error and vexation of spirit, and the work is done more or less blindly, quite in ignorance of the why and the wherefore.

Standard Methods of Analysis.—When different chemists present conflicting results, discord is sure to arise in settlements between buyers and sellers, and in the control of works processes. As a result, many corporations have been driven to insist on the use of certain uniform methods of analysis in testing the materials in which they are interested. The idea has been taken up seriously by a number of chemical societies, and there are now quite a number of so-called "Official or Standard Methods of Analysis" for particular substances—*e.g.* fertilisers, food-stuffs, etc. (*vide* page 250). The idea is to secure concordant analyses, to reduce errors to a minimum, and to place commercial analytical practice on a higher plane. The proposed methods are not fixed for all time, but are revised periodically so as to substitute improved methods when such are available.

Standardised Samples.—In 1905, the American Foundryman's Association prepared with great care a set of samples of iron, had them analysed by three or four chemists of recognised ability, and sold portions as "standardised samples" at a reasonable price. The idea has since been further elaborated by the Bureau of Standards, Washington, U.S.A., from which "standardised samples" with detailed certificates of analysis can be obtained. The work has up to the present been largely restricted to alloys and ores of various kinds.[2] Standardised samples of clay can be obtained from the County Pottery Laboratory, Stoke-on-Trent, at 10s. 6d. per 100 grams. Some of the uses of standardised samples are as follows:

(1) An analyst unfamiliar with a particular analytical process can practise with the analysed samples until he is perfected. The standardised samples also furnish useful checks for advanced students of quantitative analysis.

(2) The applicability and accuracy of a new or "improved" method of analysis can be determined with comparatively little effort by working with standardised samples.

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[1] H. S. Washington, *Prof. Paper U.S. Geol. Sur.*, **14.** 14, 1903.

[2] *Circular Bur. Standards* **25.** 3, 1912; **26.** 3, 1910; **40.** 3, 1912; W. F. Hillebrand, *Journ. Ind. Eng. Chem.*, **1.** 41, 1909; W. C. Ebaugh, *ib.*, **1.** 63, 1909; L. C. Jones, *ib.*, **1.** 269, 1909; W. D. Richardson, *ib.*, **1.** 5, 1909.

(3) In cases of disputed results, owing to the use of faulty methods of analysis by one of the chemists, both parties can analyse a standardised sample, and find who is at fault before the case comes into court. This seems more satisfactory than submitting the original sample to a third party as umpire, because the umpire may be no more capable than the contending analysts.

The Evolution of Modern Analytical Practice.

How Analytical Processes have Grown.—A comparison of the classical text-books of H. Rose (1829), C. F. Rammelsberg (1845), C. R. Fresenius (1841–6), C. F. Mohr (1855), and L. E. Rivot (1861–6) with those published in more recent years shows that the development of the art has been painfully slow. Many, perhaps most, of the standard processes are purely empirical or rule-of-thumb. The original methods devised by the fathers of analytical chemistry gave more or less approximate results; with increasing experience, these processes were modified—now here, now there—until methods were evolved which would furnish results accurate within the limits of experimental error tolerated in practice. The methods now in vogue for dealing with the so-called rare earths are in the earlier stages of the evolutionary process; while the elaboration of the regular methods for the determination of phosphorus, magnesia, sulphur, and potassium; the chromate process for the separation of barium and strontium; the sulphide processes for the separation of antimony and tin, and for the separation of zinc; and the well-known basic acetate process, all bear eloquent testimony to the adventitious and empirical way the art has developed. Much work has been directed to developing speed without sacrificing accuracy, and towards determining one or two constituents in a mixture, and ignoring the others. Hence, some industrial routine processes have been abridged (mechanicalised) into a rigid code of instructions such that boys or girls—"testers," as they are called,—of no special education or preparation, can be taught in a short time to perform the necessary operations and get good results.

The Substitution of New Processes.—Owing to the curious evolution of the processes used in analytical chemistry, analysts are reasonably reluctant in introducing new methods. It is not wise to substitute comparatively untried processes—however promising they may appear—without very careful consideration. The dread of incorporating unknown errors in our work begets caution,

> And makes us rather bear those ills we have
> Than fly to others that we know not of.

In an old, long-tried process, the disturbing factors and the precautions necessary for accurate work are fairly well known, whereas with a novel process much has to be learned in humouring its little idiosyncrasies in order that it may furnish the best results. In spite of this conservatism, several new processes seem to be gradually ousting many of the older methods, and winning their way into general practice. The reagent list is accordingly extending to include hydroxylamine, hydrazine, nitroso-β-naphthol, α-dimethylglyoxime, nitrosophenylhydroxylamine, etc. Indeed, many separations can be expedited by some of the newer methods, which are accordingly often recommended in preference to the older processes.

Class Exercises.—The need for humouring the different analytical processes is seldom taught in the schools. The beginner, working through routine class exercises with fairly pure substances, or with commercial materials whose composition has not been checked, gets little or no inkling of the difficulties which dog the footsteps of those who apply these methods to industrial products under industrial conditions, working against time. The early simple exercises are of course indispensable for training the hands of the neophyte in the operations of weighing, filtration, washing precipitates, etc.; and it is here assumed that these exercises have done the work which is expected from them, so that we can take up our studies presupposing a certain amount of knowledge of general and analytical chemistry, and more particularly of qualitative analysis. In Part I. of this book, however, the instructions for the fundamental operations have been revised in order to introduce hints and "tips" which are often left to be "picked up," if at all, in a random, haphazard way. A study of experimental errors is also of fundamental importance to an analyst who takes an interest in his work, and who is something more than a mere tester.

The Variety and Diversity of the Work in the Silicate Industries.—The methods of analysis for clays and related silicates are fairly general, and require little or no modification from sample to sample; it has therefore been possible to give a detailed scheme for their analysis in Part II., and this is used as a standard of reference for the remainder of the book. The case is very different with glazes and enamels, for it is not often that two consecutive analyses can be conducted by exactly the same method; the change in method from sample to sample is still more pronounced in dealing with colours. Some of the materials submitted for analysis involve extremely difficult separations, and a special method must be devised to suit each case. Sometimes, too, the report of the analysis has to be accompanied by a working recipe, and, with the more delicate colours, this is a severe test of the accuracy of the work. In our laboratory, for example, an enamel containing arsenic, antimony, tin, and fluorine was once followed by a black colour containing iron, chromium, manganese, cobalt, and zinc; and this, in turn, by a pink colour containing gold, silver, tin, and lead. In each case, these elements were accompanied by the ubiquitous silica, alumina, alkalies, and alkaline earths, and, in three cases, by boric oxide. There was also an inquiry for an examination of a faulty oleaginous platinum lustre for elements of the platinum group other than platinum.

Unfamiliar Operations.—Although the proportion of analyses of complex mixtures of the kind just indicated to analyses of clays, bricks, and related materials, which are required from a laboratory which specialises in this kind of work, averages over one in thirty, yet it would be a mistake to cut down the directions for the analysis of the less frequently occurring substances because of their rarity. On the contrary, fuller minutiæ are then required, because, the less familiar the road, the greater the need for guide-posts and danger signals, and the greater the probability of "accidental errors." So many cases have arisen where schemes for the analysis of unfamiliar mixtures are not included among those given as types in text-books on quantitative analysis, that much time must have been wasted in devising feasible processes, even when a good library is available. It is quite impracticable to describe methods suited to every possible or likely case which might be required in practice; nor did it seem to me so expedient to give detailed schemes for a few mixtures as to take an imaginary mixture, more complex than would obtain in practice, and indicate the short-cuts to be made when the qualitative analysis shows that the conditions are favourable. It is thus nearly always possible to curtail the general schemes—pages 319, 387, 439, 509—to suit particular cases, of course bearing in mind the hints given on page 278.

The Theory of Analytical Operations.—The *technique* of analytical chemistry has been worked out without much aid from theory, for the classical text-books have merely elaborated details of manipulation necessary for exact results. In 1894, W. Ostwald demonstrated the important bearing which the theories of physical chemistry have upon the practice of analytical chemistry. Opinions may differ very much as to the function of the *ionic hypothesis* in analytical chemistry, and whether anything is really gained by describing the facts of an essentially practical art in the language of a very hypothetical doctrine. Excluding this hypothesis, perhaps the most important ideas derived from physical chemistry which have tempered analytical operations are: (1) The theory of *adsorption* (pages 97, 179, 611, etc.). It seems to be impossible to wash a precipitate perfectly free from adsorbed liquids or solids, although it is usually possible to make the error so introduced negligibly small. (2) The laws of *the colloidal state of matter* (pages 96, 212, 275, etc.). When an "insoluble" precipitate separates from a solution in the absence of dissolved electrolytes, it is frequently in the colloidal condition, and it cannot then be isolated by filtration and washing. An electrolyte must be added in order to get the substance in a condition suited for treatment. (3) The theory of *incomplete reactions* (pages 181, 272, etc.). The reactions which result in precipitation and neutralisation are not usually complete. Instead of running to an end, the system takes up a state of equilibrium between the initial (or solution) stage and the final (or precipitate) stage, and a certain amount of the element under investigation escapes precipitation. Perfect separations by precipitation are not therefore possible, and consequently it is desirable to study each process with the object of finding the conditions necessary to make the precipitation complete enough for practical requirements. This is partly what is meant above by "humouring an analytical process."

PART I.

GENERAL.

CHAPTER I.

WEIGHING.

§ 1. The Balance.

The balance is one of the most important instruments used by the analytical chemist. It is essentially an instrument for comparing weights. The object of weighing is to compare the quantity of matter in a given substance with the quantity of matter in a standard substance—the weight or weights. The comparison is made on the balance by suspending the object to be weighed at one end of a beam supported at the middle by a pillar. The weights are suspended at the opposite end of the beam. The beam is virtually a kind of lever, and the mechanical theory of the balance is mainly founded on the properties of levers.[1]

The beam of the balance rests on a central knife-edge, generally of agate, which presses against a plane agate bearing fitted to the beam. This arrangement acts as the fulcrum of a lever of the first class. Two pans for supporting the masses to be compared are suspended from stirrups, each of which has an agate plate which rests on a knife-edge fixed at each extremity of the beam. Each arm of the balance is so graduated that pieces of wire[2]—riders—of known weight can be placed on the beam at any required distance from the central knife-edge. The rider is used instead of weights below a centigram—0·01 grm.

If the three knife-edges press continually against their agate bearings, they soon become blunted, and wear furrows in the bearings. When this occurs, the balance is inaccurate, and must be laid up for repairs. In order to prolong the life of the knife-edges and bearings as much as possible, every balance should be provided with an "arrest," which separates the three knife-edges from their bearings when the balance is not in use. The "arrest" is usually worked from the front or left side of the balance. Great pains are taken by the makers to reduce the friction upon the knife-edges to a minimum. When the balance shows signs of stiffness in the motions of beam and pans, the fault should be investigated at once. The defect may be due to an accumulation of dust between the knife-edges and their bearings; to the rusting of the knife-edges, if made of steel; to the blunting of the knife-edges; or to the wearing of furrows in the bearings. To prevent dust accumulating on the knife-edges, etc., the balance is enclosed in a glass case.

Small movements of the beam are scarcely perceptible, and consequently the beam is provided with a long pointer which multiplies the rotational displacement. When equilibrium is established, the pointer rests in front of the zero of a scale cut in a piece of ivory. Instead of taking the centre of the scale as

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[1] The theory of the balance is usually discussed in text-books on physics. The student is referred to J. Walker, *The Theory and Use of a Physical Balance*, Oxford, 1887; E. Brauer, *The Construction of the Balance*, London, 1909; W. S. Aldis, *Trans. Newcastle Chem. Soc.*, **3.** 151, 161, 1876.

[2] The rider is said to have been devised by J. J. Berzelius—P. Schwirkus, *Zeit. Instr.*, **6.** 42, 1887.

"zero," it will be found more convenient, later on, to number the scale 0 to 20, starting from the left, as indicated in fig. 6. In that case, "10" will be the "zero"—the position of rest—of the balance. There are several other adjusting devices and conveniences, which vary with different balances made by the same or different manufacturers.[1]

Whatever balance be selected, the operator must make himself perfectly familiar with its peculiarities. The conditions which must be satisfied by a good balance are:—

(1) The balance must be consistent. It must give the same result in successive weighings of the same body. This condition depends upon the accuracy of the knife-edges.

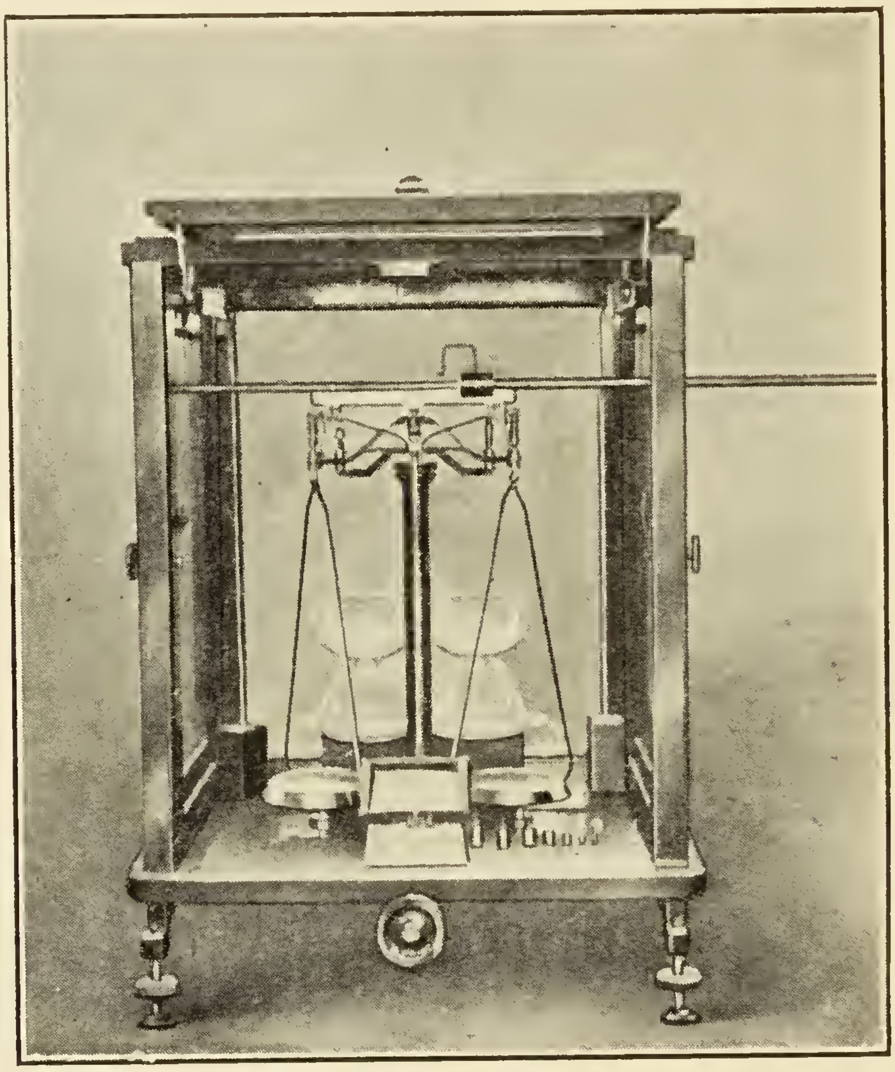

Fig. 1.—Sartorius' balance.

(2) The balance must be accurate. The beam must be horizontal when the pans are empty, and when equal masses are placed on the pans. This condition depends upon the equality of the two arms. To eliminate any error arising from the inequality of the arms of the beam, see page 21.

(3) The balance must be stable. The beam after being displaced from its horizontal position must return to its horizontal position. This condition depends on the adjustment of the centre of gravity; see below.

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[1] A balance suitable for analytical work may be obtained from £8 upwards. £10 will purchase an excellent balance. The eight-guinea balance of Sartorius, represented in fig. 1, is quite satisfactory for general analytical work, but other makers' balances, as cheap, may be equally good. The mechanism under the floor of the balance can be protected from dust, etc., by a wooden cover at a cost of two or three shillings more. Among the more important makers are F. E. Becker, Rotterdam; P. Bunge, Hamburg; L. Oertling, London; A. Rueprecht, Vienna; F. Sartorius, Göttingen. These and other makers' catalogues might be consulted before purchasing. If possible, get a balance of nearly constant sensibility. The weights will cost 25s. or more. A cheaper balance and set of weights are also necessary for weighing reagents, etc., where great accuracy is not needed.

(4) The balance must be sensitive. The balance must show any inequality in the two masses on the scale pans even when the differences are small.

(5) The balance beam must oscillate quickly. The time taken for an oscillation of the beam, as indicated by the pointer, should be as small as possible, in order that the weighing may be done quickly.

§ 2. An Outline of the Theory of the Balance.

Let AOB, fig. 2, represent the beam of a balance,[1] and let the beam be so fixed that it moves freely about the axis or central knife-edge O. Let A and B represent terminal knife-edges. Let the centre of gravity G of the system be below the axis O,[2] and let W denote the weight of the beam, and let the pans be loaded with equal weights P. Suppose an excess of weight p be placed on the right pan. The balance will then turn through a certain angle α so that A passes to A', B to B', and G to G'. The weight of the beam now acts at G', and tends to bring the beam back to its horizontal position. In consequence of the resistance of the axis O, the two weights P neutralise one another, and the weight p applied at B' and the weight W applied at G' remain. These two forces are parallel and in equilibrium about the axis O, so that their resultant passes through O. Then, from the principle of levers,

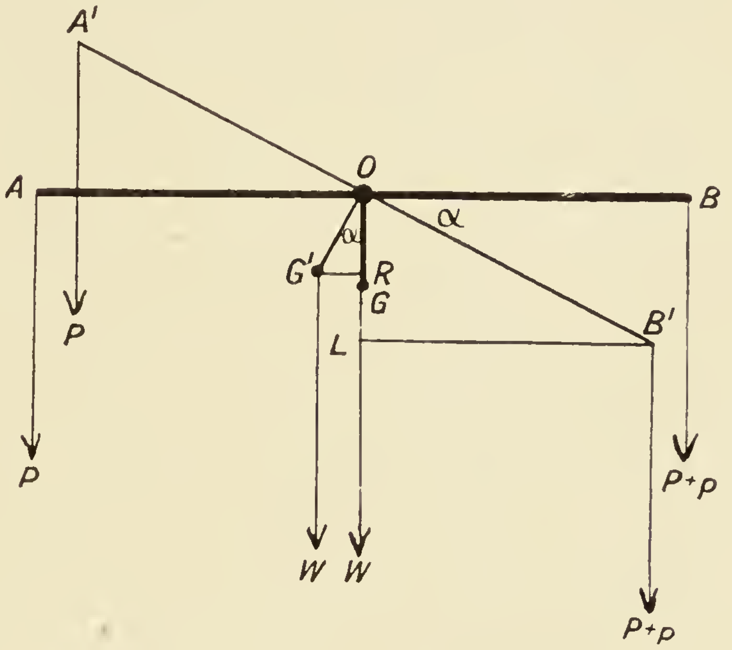

Fig. 2.—Theory of the balance.

$$W.G'R=p.B'L.$$

Let l denote the length of each arm, AO and OB. Then, $B'L=l\cos\alpha$. Let $OG=OG'=r$. Then $G'R=r\sin\alpha$. Hence, $Wr.\sin\alpha=pl.\cos\alpha$. Or,

$$Wr\tan\alpha=pl.$$

This formula embodies the theory of the *sensibility* of the balance. When the deflections are small, α may be written in place of $\tan\alpha$.[3] Hence, the

$$\text{Angle of deflection}=\frac{pl}{Wr}\,.$$

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[1] It is here assumed that the central knife-edge is in the same straight line as the terminal knife-edges. If not, it can be shown (1) that the sensibility of the balance is dependent on the load; and (2) that the balance is liable to take up a position of unstable equilibrium. Some of the more elaborate and expensive balances provide for the adjustment of the three points of suspension—terminal and central knife-edges. M. Thiesen, *Zeit. Instr.*, 2. 359, 1882; 3. 81, 1883; F. Sartorius, *ib.*, 2. 385, 1882.

[2] If the centre of gravity G be above the central knife-edge O, the beam will be in unstable equilibrium, and the slightest addition of weight to either scale pan will lead the beam to turn upside down. The balance is then said to be "cranky." If G coincides with O, the beam will be in a state of neutral equilibrium and it will rest in any position.

[3] It is convenient to measure the angle in terms of the divisions of the scale (fig. 6). This is sufficient for practical requirements—M. Thiesen, *Trav. Bur. Int. Poids. Mes.*, 5. 2, 1886: G. Schwirkus, *Zeit. Instr.*, 7. 41, 83, 412, 1887. For a discussion on this subject, see A. Bachinskii, *Zeit. phys. chem. Unterricht.*, 24. 24, 1911; O. Hartmann and Pforzheim, *ib.* 24. 93, 1911.

From this relation it follows that the angle through which the balance turns for a given difference of weight p depends upon

(1) The length of the beam, l. The longer the beam, the greater the sensibility.

(2) The weight of the beam W. The lighter the beam, the greater the sensibility.

(3) The distance, r, between the central knife-edge and the centre of gravity. The closer the centre of gravity to the central knife-edge or point of suspension of the balance, the greater the sensibility. The position of the centre of gravity is regulated by the "gravity bob" (page 14).

Obviously, it is necessary to make a compromise between these opposing qualities. For instance, if the arms are lengthened, the beam is made heavier.[1]

From the theory of the compound pendulum, it can be shown that the time required for a single small oscillation of the beam is equal to $C\sqrt{S}$, where C is a constant for a given balance carrying a particular load, and S represents the sensibility of the balance. Hence, for a given load, the time of oscillation varies directly as the square root of the sensibility. It is important to make the period of vibration as short as possible, in order that too much time may not be consumed in weighing. The time of oscillation may be taken to represent the *stability* of the balance. Consequently, high stability can only be obtained by sacrificing sensibility.[2] Hence, the greater the distance of the centre of gravity G from the axis O, and the longer and heavier the beam, the longer the time of oscillation and the less the stability of the balance. Here again we are confronted with opposing qualities.

The balance must be adjusted so that the length, strength, weight, and location of the centre of gravity of the beam may produce the maximum sensibility, stability, rapidity, and strength requisite for a specific purpose. This is a problem for the manufacturer, and need not be discussed further. The solution of the problem has led to the manufacture of two classes of balance—short-beam and long-beam.

§ 3. The Location, Care, and Use of the Balance.

If the balance be in danger of vibrations, shocks, or jars while in use, it should be placed on a firm foundation—either on solid masonry built from the ground, or isolated from the floor vibrations by resting it on a shelf fixed to heavy brackets against the walls, and not with legs resting on the floor. The balance should be adjusted perfectly horizontal by means of levelling screws outside the balance case and a spirit level or plumb bob inside the case.

The balance should be located so that it is not likely to be heated unequally,[3] and therefore it should not be placed near a door frequently opened, nor adjacent to a stove, hot-water pipe, window, or ventilating shaft. If the location be not suitable, the "zero point" of the balance will be continually changing owing to the unequal expansion of the arms. If possible, the balance should be kept in a separate room. If a small room cannot be partitioned off from the laboratory, a second glass case covering the balance case proper may be needed. Keep the mechanism free from dust. Hence, the balance case must not be opened in a dusty room. If artificial light be employed, it should be above and at the back—if possible, over the right shoulder—of the operator.

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[1] And the beam also loses rigidity. If the terminal knife-edges are above the central knife-edge, and the beam is slightly bent by a load, there will be an increased sensibility with increase of load until the three knife-edges are in the same straight line. After that any further lowering of the terminal knife-edges will diminish the sensibility (B. S. Proctor, *Trans. Newcastle Chem. Soc.*, **3**. 183, 1876 ; *Chem. News*, **34**. 14, 1876). The beam must be made as light and as inflexible as possible. Hence, magnalium and aluminium beams, made in the form of light girders, are common.

[2] Time is wasted in protracted weighings, and there is a great danger of an absorption of moisture by certain powders during the operation.

[3] If one arm be 1° hotter than the other, the error introduced in a weighing amounts to about 0·001 grm. on a 50-grm. load, and proportionally less for a smaller load. W. H. Miller (*Phil. Trans.*, **146**. 753, 1856) detected a difference of 0·00001 mm. in the thermal expansion of the two arms arising from a change in the temperature of the room. The arms expanded unequally owing to a difference in the quality of the metal forming the beam. T. Middel, *Drude's Ann.*, **2**. 115, 1900 ; P. Schwirkns, *Zeit. Instr.*, **7**. 42, 1887 ; J. J. Manley, *Trans. Roy. Soc.*, **210**. A, 387, 1910.

If there be any likelihood of the atmosphere in the vicinity of the balance being contaminated with acid fumes, lime and alkaline carbonates should be kept in the balance case to neutralise their effects. Calcium chloride is frequently kept inside the balance case in glass vessels made for the purpose,[1] or in a funnel, which in turn rests in an Erlenmeyer's flask. The idea is to keep the atmosphere inside the case dry. The remedy is by no means effective, as will be shown later. A mixture of fragments of quicklime and granulated calcium chloride is good. Some object to the use of concentrated sulphuric acid as a desiccating agent in the balance case owing to the fumes (sulphur dioxide) which are given off when organic dust collects in the acid jar.[2]

The operator should sit in front of the balance case, so as to avoid errors due to parallax in the reading of the pointer. Move the release and arrest screw with a slow, steady motion, not in jerks, since a jerky motion injures the knife-edges. The mechanism should work smoothly, and the "pan arrests" should touch the pans when the beam is lowered. When the beam is raised, the pointer should swing at equal distances, or very nearly equal distances, on each side of the zero. If not, the balance pans should be brushed free from dust, etc., by means of a camel-hair brush.[3] It may, however, be necessary to restore the equilibrium of the beam by adjusting the proper screws.[4] The beam and pans must always be arrested before any change is made in the load or weights on the pans. The object to be weighed and the heavy weights should be placed in the middle of their respective pans, since a heavy load near the edge of the pan sometimes causes troublesome oscillations not easily stilled. The balance case should be closed while weighing with the rider, so as to avoid currents of air. If the beam does not swing when released, it may be set in motion by using the hand as a fan to waft a gentle puff of air on to one of the pans.[5] There is a "trick" in lowering the beam supports so that the oscillations of the pointer will have the required amplitude.

The object to be weighed should neither be (1) hotter, nor (2) colder than the atmosphere in the balance case. Currents of hot air may impinge on the arms of the balance and cause one arm to expand unequally, or buoy up the beam. For instance, a platinum crucible which appeared to weigh 20·649 grms. when warm, really weighed 20·692 grms. when cold. Hence, the crucible weighed 0·2 per cent. less when hot than cold. If the crucible be colder than the atmosphere of the balance case, moisture may condense on the object to be weighed. If the object to be weighed is likely to be electrified, it should be allowed to stand some time after it has been wiped, before it is weighed.[6]

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[1] Two are shown in fig. 1.

[2] G. S. Johnson, *Chem. News*, 68. 211, 1893.

[3] If anything solid or liquid be spilt on the pans or in the balance case, clean it off at once.

[4] Usually, a small pennant is placed near the top of the pointer, or screws at or near the ends of the beam, for this adjustment. These screws should be interfered with as seldom as possible.

[5] If the movements of the beam seem to be erratic, the fault is probably due to (1) the beam touching the rider or the carrier of the rider; or (2) the pan touching some object in the balance case; or (3) a displaced stirrup.

[6] J. A. R. Newlands, *Chem. News*, 11. 107, 1865.

The electrification of the weights[1] or object causes erratic movements of the pointer.

The balance should not be cleaned too frequently. With proper care, and the balance in a suitable position, a good cleaning every three or four months should suffice. This may occupy from a quarter to an hour. All the loose parts should be carefully removed and dusted; the movable parts, cleaned and oiled. Wipe off any excess of oil. Polish the suspensions with a piece of chamois leather. Restore all the parts. Adjust the equilibrium screws and gravity bob as indicated later in this chapter. The weights can be tested at the same time.

§ 4. Weighing Hygroscopic or Volatile Liquids and Powders.

Never place solid reagents in direct contact with the pans. Small crucibles, watch-glasses, basins, capsules, glazed paper,[2] etc., are convenient supports for substances not affected by exposure to the air while being weighed. Hygroscopic, efflorescent, and volatile substances, and substances liable to absorb carbon dioxide, etc., from the air, must, if possible, be weighed in closed vessels, clipped watch-glasses with ground edges, etc. A selection of such vessels is shown in the diagram, fig. 3. The weighing bottle or tube must be adapted for the material under investigation. Weighing tubes must be suitably supported. The stand shown in the diagram, fig. 3*a*, is suitable for supporting a tube either vertically or horizontally. The weighing tube may be permanently closed at one end, and fitted with a ground stopper at the other—fig. 3*a*; or it may have a ground cap at both ends—fig. 3*f*. Weighing tubes for boats may have two legs to prevent rolling—fig. 3*g*.[3] Watch-glasses with ground close-fitting edges are

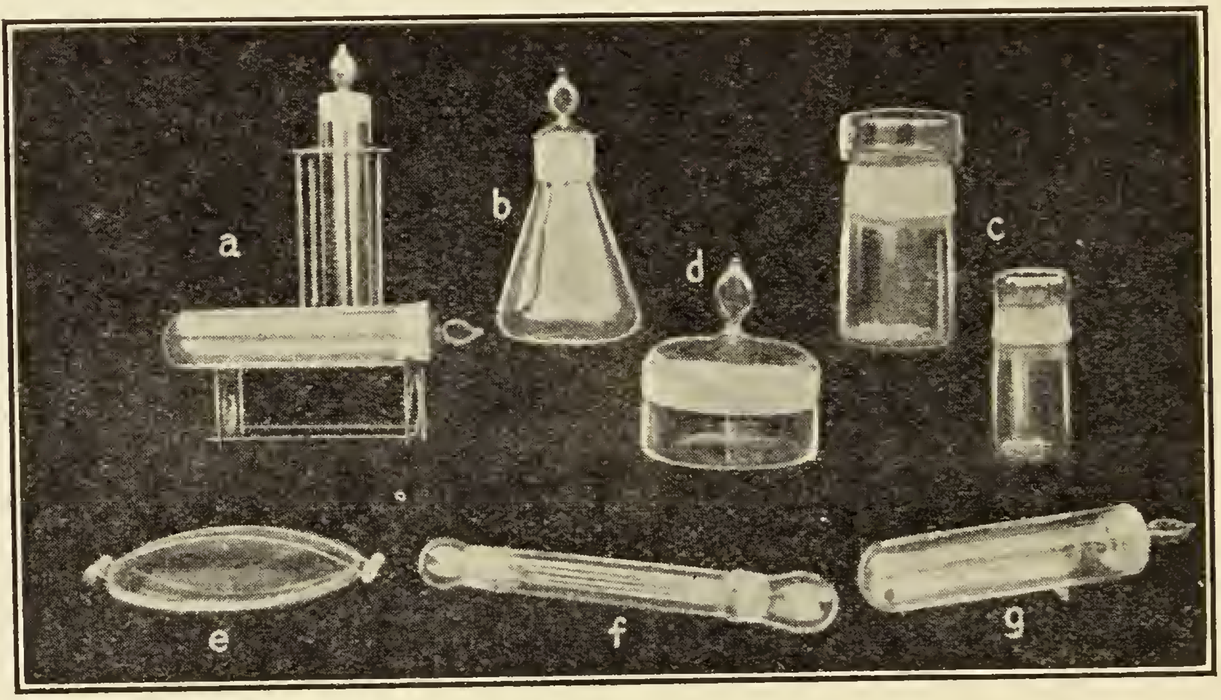

FIG. 3.—Weighing bottles and weighing tubes.

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[1] Quartz weights (H. Buff, *Dingler's Journ.*, **222**. 159, 1878; S. Stein, *Zeit. anal. Chem.*, **17**. 471, 1878; glass weights—R. Ulbricht, *Ber.*, **10**. 129, 1877) in a velvet-lined box are liable to become electrified as they are removed from their bed (*Chem. Ztg.*, **12**. 494, 1888). See page 551. R. Hennig (*Zeit. Instr.*, **5**. 161, 1886) discusses the errors due to air currents which are set up when liquids are weighed in open vessels.

[2] Paper, horn capsules, and similar substances are somewhat hygroscopic and vary in weight with the humidity of the air. "Xylonite paper" has many advantages over ordinary glazed paper. It is less hygroscopic; it can be washed with water; it is not attacked by ordinary acids and alkalies. It is attacked by organic solvents (H. Schweitzer, *Chem. Ztg.*, **14**. 698, 1890). H. F. von Jüptner, *Die Einführen einheitlicher Analysenmethoden*, Stuttgart, 261, 1896. I keep weighing bottles, brushes, etc., in a glass "catgut" box beside the balance.

[3] A. Gawalovski, *Chem. Centr.* (3), **16**. 369, 1886.

clamped together by a suitable clip as shown in the diagram—fig. *3e*.[1] Weighing bottles may have different shapes and sizes—figs. *3b*, *3c*, *3d*. They may have ordinary ground stoppers, or ground caps as in Guttmann's weighing bottle—fig. *3c*. The latter are best for powders,[2] in weighing by difference, since (1) several portions can be weighed out successively without the joint having to be cleaned, as is necessary with the ordinary ground stopper, and (2) dust does not accumulate between the stopper and the ground surfaces. A modification with ground-in tubes is useful for drying substances in a current of gas, for determining water of crystallisation, etc.—fig. 182.

In using weighing bottles or tubes, the vessel plus powder may be weighed. Some powder is removed from the vessel, and the vessel and powder weighed again. The loss in weight represents the powder removed. The capped weighing bottle may also be used for weighing liquids—fig. 4. The tube with the liquid has a small pipette inside. All is weighed. Some liquid is withdrawn by means of the pipette.[3] The pipette is returned to the bottle, and all is weighed again. The loss in weight represents the amount of liquid removed. Berl[4] has a convenient pipette for weighing corrosive liquids—fig. 5. The apparatus is weighed. The tap *C* fits closely without lubrication. To fill the pipette, connect *A* with *K*; apply suction at *A*, close *C*. Let the point *S* dip in the liquid under examination; connect *P* and *K*. The liquid runs into the pipette. Close the tap before the liquid has reached the tap *C*. Clean the end of the tube *S*. Return the pipette to the tube *F* and weigh. The increase in weight represents the amount of liquid in the pipette. Now let the tip *S* dip under water. Let the contents gradually run from the pipette by opening the cocks. Run water through the apparatus. This will ensure the removal of all the liquid from the pipette.[5] This procedure may be obviously modified to suit particular conditions.[6] The instrument is rather lighter than Lunge and Rey's well-known pipette for a similar purpose.

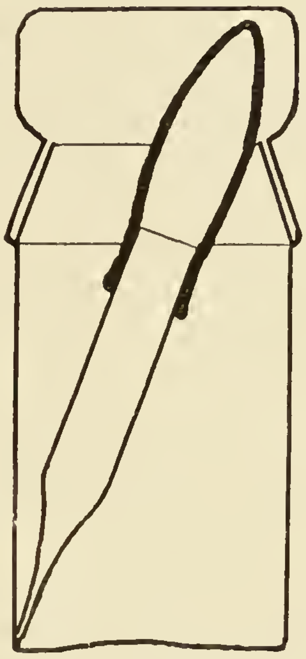

Fig. 4.—Weighing bottle and pipette.

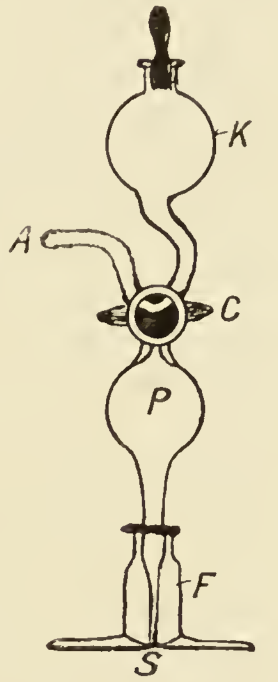

Fig. 5.—Berl's weighing pipette.

Large glass and porcelain vessels, platinum crucibles, basins, etc., dried and cooled in desiccators are particularly liable to condense moisture on their surface while being weighed.[7] Many powdered substances also begin to absorb moisture and possibly also other gases quite energetically immediately they have left the desiccator, and Pagasogli[1] mentions an example where a powder dried over sulphuric acid increased in weight from 0·001 to 0·003 grm. during the weighing, which occupied between 3 and 6 minutes. The weight of a body will increase until the vapour pressure of the absorbed moisture is equal to the vapour pressure of the moisture of the air. A dish of concentrated sulphuric acid, or a vessel[2] of ground calcium chloride, is usually kept in the balance case with the idea of retarding the absorption of moisture while the substance is being weighed. The remedy, however, is not particularly efficacious. This is well illustrated by the following observations:[3]—A hair hygrometer was placed in a balance case. Some fresh granulated calcium chloride was placed in a funnel resting over a flask. The hygrometer showed a humidity of 60·5 to 61 per cent. In an hour, the humidity fell to 55·5 per cent.; in 15 hours, to 53·5 per cent. The humidity then gradually rose during the next three days to its former value, 60–61 per cent. The calcium chloride was then appreciably moist, and liquid began to drop from the funnel containing the salt in question.

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[1] J. J. Griffin, *Chem. News*, 101. 71, 1910.

[2] C. Mangold, *Zeit. angew. Chem.*, 4. 441, 1891; L. F. Guttmann, *Journ. Amer. Chem. Soc.*, 28. 1667, 1906; A. Breneman, *Chem. News*, 48. 168, 1883; T. Zöhren, *Chem. Ztg.*, 36. 824, 1912.

[3] For a weighing bottle with a pipette stopper, see L. E. Levi, *Journ. Amer. Chem. Soc.*, 27. 614, 1905.

[4] G. Lunge and H. Rey, *Zeit. angew. Chem.*, 4. 702, 1891; H. Rosenlecher, *Zeit. anal. Chem.*, 37. 209, 1898; E. Berl, *Chem. Ztg.*, 34. 428, 1910.

[5] For strong fuming acids, a drop of liquid may escape from *S* into the tube *F* while it is being weighed. In that case, a drop of water is placed in *F*, and all is weighed without allowing the tip of the tube *S* to be wetted. The pipette is then filled as described in the text. Berl has modified bulb for liquids with a high vapour tension (*i.e.* volatile liquids).

[6] When weighing liquids which spoil on exposure to the air, Holde's pipette may be used. D. Holde, *Zeit. angew. Chem.*, 12, 711, 1899; H. Schweitzer, *Journ. Amer. Chem. Soc.*, 15. 190, 1893; E. Reichardt, *Zeit. anal. Chem.*, 7. 187, 1868.

[7] Vessels full of air have a uniform weight as soon as their surfaces are in equilibrium with the atmosphere. When these conditions are changed—by a variation of temperature for

Ostwald[4] recommends weighing the substance as rapidly as possible after removing the vessel from the desiccator. The idea is to make the error due to adsorption as small as possible. In igniting, drying, etc., to a constant weight the same time may not always be occupied in making the control weighings, and different results may accordingly be obtained with the same body. For instance, three control weighings of the same body gave 17·4334, 17·4332, and 17·4331. The idea is best applied by getting the approximate weight of the dried body in a covered crucible. Repeat the ignition and cooling, place the necessary weights on the pan, so that the rider alone is needed to complete the weighing. This will usually suffice, but a third ignition and drying will enable the third weighing to be made in a few seconds.

On the other hand, Smith[5] recommends leaving the body 20 minutes in the balance case after it has been removed from the desiccator, in order that the body may adsorb its normal film of moisture, *i.e.* until its weight is constant. The objection to this plan is the long time required for the control weighings, and there is nothing to show that the atmosphere has remained of a constant humidity during the experiment. However, it is not likely to change appreciably under ordinary conditions.[6]

§ 5. Weighing.

Weighings smaller than 0·01 grm. are made with the rider. The milligram weights are not used. When each arm is divided into ten divisions, use a

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example,—it takes a long time to bring the vessels to their original condition. Thus, a hard glass tube, 60–80 cm. long and 2–2·5 cm. diameter, must be kept two or three hours in a balance case before its weight is constant. Glass flasks, 1 to 4 litres capacity, after having been heated or rubbed, do not attain a constant weight until they have remained in the balance case five or six hours. Polished platinum rapidly regains its primitive weight, but when the surface is more or less roughened, it attains its proper weight more slowly than glass or porcelain. J. S. Stas, *Œuvres Complètes*, Bruxelles, **1**. 317, 1894; *Chem. News*, **4**. 206, 1861; J. L. Smith, *ib.*, **31**. 55, 1875.

[1] G. Pagasogli, *L'Orosi*, **10**. 109, 1888; J. L. Smith, *Chem. News*, **31**. 55, 1875.

[2] Two calcium chloride jars are shown in the back of the balance case, fig. 1.

[3] O. Kuhn, *Chem. Ztg.*, **34**. 1097, 1108, 1910.

[4] W. Ostwald and R. Luther, *Hand- und Hülfsbuch zur Ausführung physiko-chemischer Messungen*, Leipzig, 51, 1902; London, 38, 1899.

[5] J. L. Smith, *Amer. Chemist*, **5**. 212, 1874; F. P. Treadwell, *Kurzes Lehrbuch der analytische Chemie*, Leipzig, **2**. 21, 1911; New York, 22, 1904.

[6] R. Hottinger (*Zeit. anal. Chem.*, **48**. 73, 1909) recommends plotting the increases in weight as ordinates, with time as abscissæ. The curve will be horizontal after the elapse of a few minutes. The first weighing will not be zero. The time required for the first weighing is longest; subsequent weighings occupy less time. Hottinger extrapolates for zero by continuing the curve. F. Richarz, *Verhandl. phys. Ges. Berlin*, 83, 1886.

centigram rider; if each arm be divided into twelve divisions, use a 12-milligram rider.[1] Each division on the beam then corresponds with a milligram, each of the n subdivisions with the n^{-1}th milligram. The 12-mgrm. rider enables fractions below 12 mgrm. to be weighed with the rider; the 10-mgrm. rider, fractions below 10 mgrm.[2] Some balances require a half-centigram rider. This is for use on a light scale attached to the front of the beam of the balance. The effect produced by the half-centigram rider on the auxiliary beam is the same as would be obtained with a centigram rider on the beam proper. This device is only used with the very short-beam balances where the graduations on the beam with a centigram rider would be inconveniently close.

In attempting to weigh to the tenth of a milligram, it might be thought best, at first sight, to add weights and move the rider until the pointer of the balance swings equally on both sides of the zero of the scale. It is assumed, quite correctly, that when the exact weight has been added to a properly adjusted balance, the pointer will swing the same number of divisions to the right and the left of the zero, provided it does so when the pans are empty. As a matter of fact, this method is perhaps more often in error than otherwise. It entails a frequent adjustment of the zero point of the balance, owing to unavoidable variations in the zero point.[3] Even if the position of equilibrium of the pointer with an unloaded balance be adjusted with the pointer at the zero of the scale, the zero point may change in a short time. The arms may be unequally heated, etc. By ignoring this fact, appreciable errors may creep into the work. This method of weighing, in which the rider is adjusted until the swing of the pointer of the loaded balance is nearly the same as with the unloaded balance, is very common, and it is accurate enough for most analytical work. We shall see later that the errors incidental to the methods of preparing precipitates for weighing, mask the small errors introduced by the effects just indicated.

In special cases, when weighing to the tenth of a milligram, it is important to be able to make the weighing independent of any temporary inequality of the arms, etc. Hence we have:—

(1) *Gauss' method of double weighing.*—The object is weighed first in one pan, then in the other. The square root of the product is supposed to represent the weight of the object.

(2) *Borda's method of weighing by tares.*—Here the object is balanced by a suitable tare (wire, weights, shot, potash bulb, etc.). The object is removed, and weights are added in its place until equilibrium is restored.

(3) *Method of weighing by double vibrations* (*or swings*).[4]—The following description may make the process of weighing by double vibrations appear somewhat laborious. The labour is, however, more apparent than real. Practice with the method is also an excellent way of mastering the manipulation of the balance.

First, find the zero position of the pointer, that is, the position the pointer will occupy on the scale where the balance, swinging without a load, will come to rest.

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[1] The rider enables all weights below 0·01 grm. to be discarded, and this (1) saves time and trouble; (2) ensures greater accuracy owing to the tendency of the small weights to collect dirt, etc.; (2) decreases chances of error in reading the weights on the pans; and (4) renders it possible to estimate weights to a greater degree of accuracy.

[2] The weight obtained by adjusting the rider is usually treated as if it were a weight on the pan.

[3] T. E. Thorpe, *Journ. Chem. Soc.*, **47**. 116, 1885; J. J. Manley, *Proc. Roy. Soc.*, A, **86**. 591, 1912; *Trans Roy. Soc.*, A, **212**. 227, 1912.

[4] For details see text-books on physics. J. H. Poynting, *Chem. News*, **39**. 45, 1879; *Proc. Manchester Lit. Phil. Soc.*, **18**. 33, 1879.

It would be too great a waste of time to wait until the oscillations of the pointer cease when it is possible to deduce the position directly from the distances the pointer swings to the left and right of the scale.[1] Following F. Kohlrausch,[2] I prefer to number the scale with the zero on the extreme left, not in the middle of the scale. This prevents any confusion of signs later on. Neglect the first two or three swings on account of the shock, and air currents set up when the door of the balance is closed. Take 3, 5, or 7 consecutive readings of the turning points of the swinging pointer. Take the average of the odd, and also the average of the even numbered readings. Add the two results and divide by 2. In illustration, suppose the turning points read—

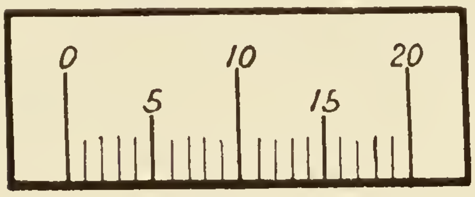

Fig. 6.—Scale of pointer of balance.

7·2; 13·0; 7·2.

The mean of the first and third readings is 7·2; the mean of both the even and odd readings is 7·2 + 13·0 divided by 2, that is, 10·1. This number represents the required zero point of the balance. The needle will come to rest when the pointer is at 10·1.[3]

Second, find the deviation of the scale per milligram, that is, the sensibility of the balance. The object to be weighed is placed on the left pan, the weights on the right pan.[4] When the weights[5] are so far adjusted[6] that another centigram weight would be too much, close the door of the balance case, and move the centigram rider on the divided beam until the pointer moves to the right and left of the 10th division. Find the position of rest, *e.g.*—

Weight on pan.	Turning points.	Averages.	Zero point.
11·216	8·2; 13·3; 8·4	8·3; 13·3	10·8

Move the rider another milligram division to the right.

Weight on pan.	Turning points.	Averages.	Zero point.
11·217	4·1; 11·6; 4·3	4·2; 11·6	7·9

Hence, the zero point is displaced 10·8 − 7·9 = 2·9 divisions by increasing the weight 1 milligram; or 2·9 scale divisions correspond with 1 milligram. This number, 2·9, represents the required sensibility of the balance for the given load. The sensibility of a balance for a given load is therefore defined as the displacement of the position of rest of the beam produced by an excess of 1 milligram weight on either pan.

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[1] The reading of the pointer in accurate work is greatly facilitated by the use of a lens or a magnifying mirror made for the purpose. The lens or mirror is so arranged that an enlarged image of the pointer and scale meets the eye when the head is in its natural position before the balance. The lens is shown in position in front of the scale, fig. 1.

[2] F. Kohlrausch, *Leitfaden der praktischen Physik*, Leipzig, 44, 1896.

[3] Scales with red lines instead of the black ones are claimed by C. M. Clark (*Journ. Amer. Chem. Soc.*, **32**. 884, 1910) to be more easily read.

[4] Keep rigorously to this rule: object on left pan, weights on right pan. The reason will appear later.

[5] The weights are not usually kept in the box, but rather on the "front floor" of the balance case. F. Clowes and J. B. Coleman (*Quantitative Chemical Analysis*, London, 4, 1909) recommend keeping the weights on a piece of cardboard ruled in squares and numbered to correspond with the weights to be kept thereon. Small porcelain slabs with suitable depressions, and properly lettered, are more convenient. Weights over, say, 20 grms. may not be needed very frequently; in that case, keep them in the box. The milligram weights are redundant, and may also be left in the box. For the condensation of "moist air" on the weights, see T. Jhmori (*Wied. Ann.*, **31**. 1006, 1887) and E. Warburg (*ib.*, **27**. 481, 1886).

[6] The weights are not to be handled with the fingers, but always lifted with the ivory-tipped forceps provided for that purpose. Never alter the load on either pan without first arresting the balance, so that the beam or stirrups no longer rest on the knife-edges.

Third, calculate the weight of the load on the pan. From the preceding results, it follows that the load weighs $11·216 + x$. The zero point of this load is displaced $10·8 - 10·1 = 0·7$ scale divisions. Since 2·9 scale divisions correspond with 1 milligram, 0·7 scale divisions will correspond with $0·7 \div 2·9 = 0·24$ scale divisions or 0·24 mgrm. Hence the weight of the body is $11·216 + 0·00024 = 11·21624$ grms. These calculations may be summarised in the formula

$$\text{Correction} = +\frac{a - z}{a - b}\text{ mgrm.},$$

where z represents the zero point of the unloaded balance; a, the zero point with not quite sufficient weight on the right pan; and b, the zero point with a milligram more on the right pan than corresponds with a.

Analytical balances will rarely indicate with certainty smaller weights than 0·0001 grm. Hence, although the weight has been stated to the fifth decimal, in future weights will generally be rounded off by dropping the fifth decimal and raising the fourth decimal one unit when the dropped figure exceeds 5. It is well to keep rigidly to one routine process, so that the preceding operations may become mechanical. With a little practice, time is saved owing to the fact that no useless trials are made in the final adjustment of the rider. The result is also more exact than the method of weighing by equal deviations of the zero point.

The following may be taken as representing the operations involved in weighing a porcelain crucible:—Add 10 grms.—too little; add 2 grms.—too much; add 1 grm—too little; add 0·5 grm.—too much; add 0·2 grm.—too little; add 0·1 grm.—too much; add 0·05 grm.—too much; add 0·02 grm.—too much; add 0·01 grm.—too little. Close the door of the balance case. Place the rider on the 5th division—too little; on the 6th division—too little, but nearly right. Read the turning points as indicated below. Place the rider on the 7th division and read the turning points. Remove the loads on the pans, and read the turning points. We thus obtain—

	Turning points.	Zero points.
Unloaded balance	7·2 ; 13·0 ; 7·2	$z = 10·1$
11·216	8·2 ; 13·3 ; 8·4	$a = 10·8$
11·217	4·1 ; 11·6 ; 4·3	$b = 7·9$

Consequently,

$$\frac{a - z}{a - b} = \frac{10·8 - 10·1}{10·8 - \ 7·9} = \frac{0·7}{2·9} = 0·24 \text{ mgrm.}$$

Hence the weight is 11·2162 grms. After a certain amount of experience has been obtained with a given balance, it is possible, before the weighing is completed, to estimate the approximate weight of the load from the rate at which the pointer moves over the scale, and thus skip some of the steps indicated for adjusting the exact weight by the process just outlined. Thus, the 0·5 grm., indicated above, was not placed on the pan during the actual weighing. This experience, however, takes some time to acquire, and it is better to work by system rather than at random.

§ 6. The Sensibility of the Balance.

Balances may now be obtained which show practically no change in sensitiveness $(a - b)$ between full and empty loads. The mere statement that "a balance is sensitive to $\frac{1}{10}$th mgrm." is not sufficient unless the corresponding load be specified. A balance carrying 5 grms. might be sensitive to $\frac{1}{10}$th mgrm., whereas $\frac{1}{10}$th mgrm. with a load of 100 grms. would have no perceptible influence on the movements of the beam.

Most balances have a "gravity bob" screw attached to the central portion of the beam, or a sliding weight on the pointer (fig. 1). The gravity bob provides a means of regulating the value of $(a-b)$, the sensitiveness of the balance, within certain limits.[1] By its means, the distance OG or r (fig. 2) between the centre of gravity and the central knife-edge can be altered. We have seen (page 6) that the nearer the centre of gravity to the central knife-edge, the greater the sensibility, and the greater the period of vibration of the balance. If the gravity bob be too near the central knife-edge, the time of vibration is too long, and the balance will be too sensitive; if the gravity bob be too far away from the central knife-edge, the balance may be unstable, either with the empty pans or with a full load. It is generally possible, by adjusting the gravity bob, to make the numerical value $(a-b)$ a single figure. Suppose, for example, we have a balance of constant sensibility so adjusted that its sensibility is 0·7, the work of weighing is much simplified. For instance, in weighing a platinum crucible, we simply find—

	Turning points.	Zero points.
Unloaded	5·4 ; 17·6 ; 5·6	$z=11{\cdot}55$
Loaded 20·023 grms. . . .	6·0 ; 18·7 ; 6·2	$a=12{\cdot}40$
Displacement of zero point		$a-z=$ 0·85

Hence, $0{\cdot}85 \div 0{\cdot}7 = 0{\cdot}12$. The required weight is 20·02312 grms. With such a balance, properly adjusted, a weighing is very quickly and accurately performed.

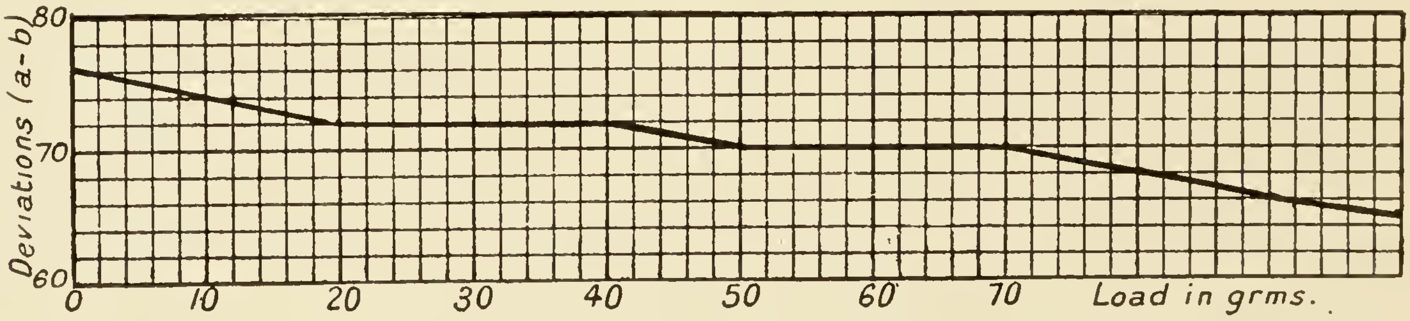

FIG. 7.—Variation of sensibility of Balance No. 3 with load.

If the sensibility of the balance varies a little with the load,[2] as is usual with common analytical balances, owing to a slight bending of the loaded beam, it is simplest to determine the value of this constant for the different loads once for all. Suppose that we find—

BALANCE No. 3.

Load . .	0,	10,	20,	30,	40,	50,	60,	70,	80,	90,	100 grms.
Deflection .	0·76,	0·74,	0·72,	0·72,	0·72,	0·70,	0·70,	0·70,	0·68,	0·66,	0·65 divs.

The value of $a-b$ can then be read at a glance, for any given load, from the graph of these numbers (fig. 7). When $a-b$ is so fixed, a and z are alone determined each weighing.

Analytical balances are now usually made with a short, light beam which has a period of vibration of about 10 seconds. The old-fashioned long-beam balances are seldom used in analytical practice. The long-beam balances sometimes have a period of vibration approaching 60 seconds; and, in consequence, a lot of valuable time may be lost in watching the oscillations of the beam, with an additional risk of error due to the absorption of moisture, etc., by the object being weighed (page

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[1] For a device for adjusting the centre of gravity, see C. Bunge, *Chem. Ztg.*, **37**. 280, 1913.

[2] H. R. Proctor, *Chem. News*, **30**. 255, 1874.

9). Short-beam balances are therefore used when rapid weighing is needed. The unavoidable errors in setting the knife-edges are of greater significance in short-beam balances; and the oscillations being small, minute differences are not so readily detected as in long-beam balances. The latter objection is partly overcome by using a lens to magnify the motions of the pointer (page 12).

§ 7. The Accuracy of the Weighing.

The finest weighing cannot compensate for the lack of purity of substance, or the absence of perfection in chemical operations.—G. D. HINRICHS.

Accurate measurement is the foundation of real science. Many students of chemistry are introduced to the art of exact measurement through quantitative analysis. It is therefore necessary to get clear ideas about the principles of measurement in analytical chemistry. It would obviously be an absurd waste of time to weigh to an accuracy of 0·001 per cent. at one stage of the work, if at another stage of the work the method of preparing the substance for weighing introduced an error of 0·5 per cent.

Although many errors are small enough to be neglected, yet cases often arise where errors, trivial under one set of conditions, assume serious dimensions under another set. Hence, it is necessary for every analyst to have clear ideas of the character of the different errors which may affect his work, in order that corrections may be introduced whenever necessary. A chemist will not consider any time lost which is necessary for obtaining accurate results; but it is certainly a waste of time to carry the accuracy of any single operation (*e.g.* weighing) much beyond the limits of experimental error incidental to the process of analysis.

Errors in weighing and measuring should fall well within the limits of the experimental error due to the analytical operations. There is no advantage in making one of a series of interdependent measurements much more accurate than the others. A chain is no stronger than its weakest link. Under ordinary conditions, ten consecutive weighings of the same substance should not differ much more than 0·0005 grm., that is, by 0·05 per cent. working with one-gram samples; whereas in other cases the error in weighing should not exceed 0·01 per cent., that is, 0·0001 grm.

EXAMPLE.—If an error no greater than 0·001 grm. were made in the initial weighing of a gram of a clay which contained 0·2 per cent. of MgO, the greatest error in the determination of the magnesia could be no greater than 0·1 per cent. of its value; and the final result could not be affected by more than 0·1 per cent. of 0·2 per cent., that is, 0·0002 gram. This is negligibly small. The weighing is even more accurate than is necessary. Suppose further that an error of 0·001 be possible in the weighing of the 0·0055 grm. of $Mg_2P_2O_7$, an error of 0·001 grm. would represent an error of $100 \times 0·001 \div 0·0055 = 18$ per cent. This is too great. The weighing must be more exact.

Clay analyses are usually made upon one-gram samples. The final result is represented as a percentage taken to the second decimal. This seems to imply that the weighings are exact to the 0·0001th of a gram. Possibly they are. It would not be very difficult to make the weighings exact to 0·00001th grm. This would enable us to represent the final analysis, as beginners frequently do, with three decimals. But we shall see that the appearance of accuracy conveyed by these decimal figures—the second and third—is quite illusory.[1] *Calculations should stop when the limit of precision of the analytical process is reached. Precision in form does not necessarily represent accurate work.*

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[1] In illustration, see the analyses of tincal by H. Vohl in *Dingler's Journ.*, **201.** 165, 1871; and of iron ores by J. C. Welch in the *Chem. News*, **52.** 32, 1885, to four places (per cent.)! This discussion is resumed later.

Altogether apart from the accuracy of the sampling, analytical operations involved in preparing the different substances for weighing are seldom more exact than is represented by Washington's[1] statement: "For silica or other constituents which amount to 30 per cent. or over, the allowable limits of error are 0·2 to 0·3 per cent. of the whole material; for alumina and other constituents which amount to from 10 to 30 per cent., 0·1 to 0·2 per cent.; and for constituents which amount to 1 to 10 per cent., 0·05 to 0·1 per cent." If we accept these numbers as representing the errors incidental to the best processes available for the analysis of silicates, clays, etc., it will be obvious that little, if anything, is gained by increasing the accuracy of the weighings beyond the tenth of a milligram, until the operations generally used in analytical chemistry admit of greater refinement. Indeed, our analyses would approximate more closely to the truth if we represented the percentage results with one decimal instead of two. As a matter of fact, two decimals are generally used in technical analyses because we have grown accustomed to the plan, not because it represents the accuracy of the work. The first decimal is supposed to be nearly right; the second is retained in order to keep the first decimal as nearly accurate as possible in calculations made with the analytical data. Under ordinary conditions, therefore, a third decimal is quite out of perspective, while a fourth is an abomination.[2]

Few analytical processes can be depended upon beyond a limit of accuracy represented by 1 in 500; still fewer beyond 1 in 1000. In fact, a method which would enable a real distinction to be drawn between 50·0 and 50·1 per cent. would be considered excellent. As a matter of fact, this degree of accuracy is seldom, if ever, attained in a complex separation. Hence, the statement that 50·13 per cent. of a constituent is present can rarely represent more accurate work than if the result had been simply expressed by the number 50·1 per cent. To quote an illustration by Hinrichs,[3] Berzelius (1826) worked with a balance accurate to 0·01 grm., Ramsay and Aston (1893) worked with a balance accurate to 0·0000001 grm. In three determinations of the water of crystallisation of borax, Ramsay and Aston found 0·471677 grm., and Berzelius, 0·4710 grm. The individual determinations in the former case varied from 0·471099 to 0·472026. Here then, with a variation in the third decimal, it follows that the fourth and succeeding decimals have no more value than the results determined on the less sensitive balance used by Berzelius.

In some cases, working under special conditions with large amounts of raw materials, it is possible to determine quantitatively certain constituents occurring in amounts below 0·01 per cent. In that case the first significant figure might appear after the second place in the final statement of the results. The determination of these constituents may be useful and important for special purposes, which are not usually industrial.

§ 8. Correcting the Weights.

When working to the tenth of a milligram, it is necessary to test an ordinary box of analytical weights in order to find if the weights are consistent amongst themselves. The errors usually permitted by a standard testing laboratory, before a first-class box of weights can receive its imprimatur, are indicated in the second column of the following table. The third column represents the degree of accuracy of the calibration.

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[1] H. S. Washington, *Manual of the Chemical Analysis of Rocks*, New York, 24, 1904; M. Dittrich, *Neues Jahrb. Min.*, **2**. 69, 1903.

[2] These remarks, of course, have no reference to the analysis of special materials under special conditions where three decimals may be needed to represent the accuracy of the work—for instance, in certain atomic weight determinations; but even here, the value of the result is frequently overrated. See C. Molar, *Rass. Min. Met. Chim.*, **36**. 101, 1912.

[3] G. D. Hinrichs, *The Absolute Weights of the Chemical Elements*, St Louis, Mo., 42, 1901.

Table I.—Permitted Errors in a Set of Weights.

Weight.	Tolerance.	Values given to	Weight.	Tolerance.	Values given to
200	0·001	0·00001	1 to 2	0·00005	0·000001
100	0·0005	0·00001	0·5	0·00004	0·000001
50	0·0003	0·00001	0·2	0·00003	0·000001
20	0·0001	0·00001	0·05 to 0·01	0·00002	0·000001
5	0·0001	0·00001			

A set of weights which has passed this test will be more accurate than is needed for most analytical work.

Fairly accurate weights can be purchased for a reasonable sum, and for most gravimetric work the inaccuracies of the better class of weights are negligibly small in comparison with the errors of experiment, and the imperfections in the processes of analysis. An analyst, however, will not be satisfied with having his weights *probably* exact enough. He must know that the weights *actually* have the required degree of accuracy. This certainty can only be established by calibrating the weights. The errors introduced by the imperfections of the weights can easily be made less than 0·0001 grm., or 0·01 per cent. The weights should be tested at periodic intervals, say every three or four months. All depends upon the frequency with which the weights are used, and who uses them. Faraday[1] has observed: "The balance and weights should be carefully examined at intervals, to ascertain their accuracy, for if they involve unnoticed errors, the experiments made with them may be worse than useless. Some curious conclusions, tending to subvert most important chemical truths, might be quoted as having arisen solely in this way." The weights should be cleaned by wiping them with a camel-hair brush, or silk handkerchief. They must not be rubbed. Two hours will suffice for the calibration.

In special cases, *e.g.* where volumetric apparatus is being calibrated, absolute weights may be required, but for general analytical work absolute weights are not necessary. For instance, suppose that 1 grm. of clay be weighed with a perfect one-gram weight, and exactly 0·1 grm. of silica is obtained. The clay contains 10 per cent. SiO_2. Suppose that the clay be weighed with a one-gram weight which is really 0·9 grm. (called 1 grm.), and that the other weights are consistent. The silica obtained would then weigh 0·09 grm. (called 0·1 grm.). Here, the amount of silica reported in the clay will be the same as before, because

$$\frac{100 \times 0{\cdot}09}{0{\cdot}9} = 10 \text{ per cent. } SiO_2.$$

Hence, *if the weights are consistent with one another, their absolute values have no influence on the accuracy of a quantitative analysis.*

Most books on analysis and physics[2] give the *modus operandi* for calibrating a set of weights. The following plan will be found to differ but little from those usually recommended. Every student beginning analytical work should be drilled by standardising a box of weights and using the method of weighing described in the preceding section.

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[1] M. Faraday, *Chemical Manipulation*, London, 29, 1842.

[2] W. H. Miller, *Phil. Trans.*, 146. 753, 1856; K. L. Bauer, *Zeit. anal. Chem.*, 8. 390, 1869; *Pogg. Ann.*, 137. 103, 1869; R. Bunsen, *Zeit. anal. Chem.*, 6. 1, 1867; T. W. Richards,

The weights are usually made in sets 1, 2, 5; and, to get the 4 and 9, it is necessary to duplicate either the 1 or the 2. German and English weights are arranged on the former system, and French weights on the latter. There is no marked difference in rapidity of manipulation with either system, *i.e.* in the average number of times the weights are removed and returned to the box during a series of weighings. With the French system, it is easier to check the weights against one another, since the $1 + 2 + 2$ should equal the 5 weight. Hence, as Pickering[1] says: "if a mistake is suspected, a test can be applied by using an additional weight instead of putting back all the small weights, and adding a larger one." To meet this objection, an extra one-gram weight is often added by the English and German makers. Weights below 0·01 grm. are not needed.

The Centigram Weights.—The rider should be rubbed with fine emery paper until it weighs exactly 10 (or 12) milligrams.[2] Suppose the box contains—

$$0{\cdot}05,\ 0{\cdot}02,\ 0{\cdot}01,\ 0{\cdot}01 \text{ gram}$$

weights. Take a centigram weight from another box, or make one from a piece of wire or foil—the weight need not be absolutely correct. It is used temporarily as a tare. Call its weight *A*. It is necessary to have some distinguishing mark for the two 0·01-grm. weights; for the two 0·1-grm. weights; for the three 1-grm. weights; and for the two 10-grm. weights. The weights may be stamped in different ways, or advantage may be taken of accidental markings; the foil weights may be distinguished by turning up different corners.[3]

Place one of the 0·01-grm. weights—say $[0{\cdot}01]_a$—on the left pan of the balance, and balance this weight with the centigram tare *A* and the rider. Suppose that we find the weights on the right $A + 0{\cdot}00000$ grm. We write down

$$[0{\cdot}01]_a = A + 0{\cdot}00000 \quad . \quad . \quad . \quad . \quad . \tag{1}$$

Replace the weight on the left with the $[0{\cdot}01]_b$ weight. Suppose we find

$$[0{\cdot}01]_b = A + 0{\cdot}00001 \quad . \quad . \quad . \quad . \quad . \tag{2}$$

Since the two weights $[0{\cdot}01]_a$ and $[0{\cdot}01]_b$ should together make up the $[0{\cdot}02]$ grm., place the two former on the right pan, and the $[0{\cdot}02]$ grm. on the left pan. We find that

$$[0{\cdot}02] = [0{\cdot}01]_a + [0{\cdot}01]_b + 0{\cdot}00002.$$

Hence, from (1) and (2), we deduce that

$$[0{\cdot}02] = 2A + 0{\cdot}00002 \quad . \quad . \quad . \quad . \quad . \tag{3}$$

Similarly,

$$[0{\cdot}05] = [0{\cdot}02] + [0{\cdot}01]_a + [0{\cdot}01]_b + A + 0{\cdot}00004,$$

Journ. Amer. Chem. Soc., **22.** 194, 1900; A. T. H. Verbeck, *Dingler's Journ.*, **227.** 400, 1878; W. Dittmar, *Exercises in Quantitative Analysis*, Glasgow, 1, 1887; W. Ostwald and R. Luther, *Hand- und Hülfsbuch zur Ausführung physiko-chemischer Messungen*, Leipzig, 55, 1902; F. Kohlrausch, *Leitfaden der praktischen Physik*, Leipzig, 50, 1896; W. Crookes, *Phil. Trans.*, **162.** 277, 1873; *Chem. News*, **15.** 191, 1867; *Select Methods in Chemical Analysis*, London, 687, 1905; H. N. Morse, *Exercises in Quantitative Analysis*, Boston, 26, 1909. For Benoit's method of calibration, see W. Watson, *A Text-book of Practical Physics*, London, 74, 1906.

[1] E. C. Pickering, *Elements of Physical Manipulation*, London, **1.** 48, 1878.

[2] Or a standard centigram rider can be purchased with, say, a National Physical Laboratory certificate.

[3] It is best to get the maker to stamp the weights of the same denomination *a*, *b*, *c* . . . before purchasing.

which, by substitution from (1), (2), (3), furnishes

$$[0{\cdot}05] = 5A + 0{\cdot}00006 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The Decigram and the Gram Weights.—The decigram weights $[0{\cdot}5]$, $[0{\cdot}2]$, $[0{\cdot}1]_a$, $[0{\cdot}1]_b$ are treated in a similar manner. We thus obtain

$$[0{\cdot}1]_a = [0{\cdot}05] + [0{\cdot}02] + [0{\cdot}01]_a + [0{\cdot}01]_b + A + 0{\cdot}0000.$$

From (1), (2), (3), (4), we get

$$[0{\cdot}1]_a = 10A + 0{\cdot}00005 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Similarly, we obtain the data for the remainder of the decigram weights, and also for the gram weights, indicated in the second column of the subjoined table:—

Table II.—Calibration Data for Weights (Student's Box No. 8).

Nominal or face value.	Data obtained in calibration.	Preliminary values assuming $A = 0{\cdot}01$ grm.	Corrected, assuming 10·00040 to be standard.	Correction. $[10]_a$ = standard.
$[0{\cdot}01]_a$	$A + 0{\cdot}00000$	0·01000	0·01000	±0·00
$[0{\cdot}01]_b$	$A + 0{\cdot}00001$	0·01001	0·01000	+0·01
$[0{\cdot}02]$	$2A + 0{\cdot}00002$	0·02002	0·02000	+0·02
$[0{\cdot}05]$	$5A + 0{\cdot}00006$	0·05006	0·05000	+0·06
$[0{\cdot}1]_a$	$10A + 0{\cdot}00005$	0·10005	0·10000	+0·05
$[0{\cdot}1]_b$	$10A + 0{\cdot}00007$	0·10007	0·10000	+0·07
$[0{\cdot}2]$	$20A + 0{\cdot}00010$	0·20010	0·20001	+0·09
[0 5]	$50A + 0{\cdot}00013$	0·50013	0·50001	+0·12
$[1]_a$	$100A + 0{\cdot}00005$	1·00005	1·00004	+0·01
$[1]_b$	$100A + 0{\cdot}00007$	1·00007	1·00004	+0·03
$[1]_c$	$100A + 0{\cdot}00007$	1·00007	1·00004	+0·03
$[2]$	$200A + 0{\cdot}00009$	2·00009	2·00008	+0·01
$[5]$	$500A + 0{\cdot}00014$	5·00014	5·00020	−0·06
$[10]_a$	$1000A + 0{\cdot}00040$	10·00040	10·00040	±0·00
$[10]_b$	$1000A + 0{\cdot}00039$	10·00039	10·00040	−0·01
$[20]$	$2000A + 0{\cdot}00070$	20·00070	20·00080	−0·10
$[50]$	$5000A + 0{\cdot}00169$	50·00169	50·00200	−0·31

We can assume *pro tem.* that A is exactly 0·01 grm., and draw up a table of corrections referring the weights, as is usually done, to the $[10]_a$ weight as a basis. This has been done in Table III., where the first column represents the normal or face value of the weights; the second column, the results expressed in terms of A; the third column, the results on the preliminary assumption that $A = 0{\cdot}01$ grm.; the fourth column, results on the assumption that the $[10]_a$-grm. weight is the standard; and the last column represents the deviations of the weights from the standard of reference $[10]_a = 10{\cdot}00040$ grm.

If desired, we can find the exact value of the $[10]_a$-grm. weight in terms of a standard 10-grm. weight. It is by no means necessary to do this. All that is necessary is that the corrected weights be consistent amongst themselves. If the $[10]_a$ and the standard 10-grm. weights are equal, the corrections in the above table need not be altered. If it were found that

$$[10]_a = 10 \text{ grm.} + 0{\cdot}00037,$$

it follows that our standard was 0·00003 grm. too high, and a corresponding change is therefore made in the table of corrections. This has been done in the following table:—

Table III.—Corrections for Weights (Student's Box No. 8).

Nominal or face value of weight.	Corrections. $[10]_a = 10$ grms. $+0{\cdot}00037$ grm.	Nominal or face value of weight.	Corrections. $[10]_a = 10$ grms. $+0{\cdot}00037$ grm.
$[0{\cdot}01]_a$	$+0{\cdot}03$	$[1]_b$	$+0{\cdot}06$
$[0{\cdot}01]_b$	$+0{\cdot}04$	$[1]_c$	$+0{\cdot}02$
$[0{\cdot}02]$	$+0{\cdot}05$	$[2]$	$-0{\cdot}08$
$[0{\cdot}05]$	$+0{\cdot}09$	$[5]$	$-0{\cdot}23$
$[0{\cdot}1]_a$	$+0{\cdot}04$	$[10]_a$	$+0{\cdot}03$
$[0{\cdot}1]_b$	$+0{\cdot}06$	$[10]_b$	$-0{\cdot}02$
$[0{\cdot}2]$	$+0{\cdot}05$	$[20]$	$-0{\cdot}07$
$[0{\cdot}5]$	$+0{\cdot}12$	$[50]$	$-0{\cdot}28$
$[1]_a$	$+0{\cdot}04$	$[100]$	$-0{\cdot}42$

It will be observed that, if the weight be not heavy enough, the correction must be subtracted from the apparent weight of the substance to be weighed. Such a correction is indicated in the table with a minus sign. Conversely, if the weight be too heavy, the correction must be added to the apparent weight of the substance. Beginners most frequently trip over this. If the corrections anywhere exceed the values indicated in the table, page 17, return the box to the makers. A good set of weights is a treasure; a bad set, an incubus.

The way to use the table of corrections will be obvious from the following example:—

	Observed weights.	Corrections.	Corrected weights.
Crucible and substance . .	29·7459	$\left\{\begin{matrix}-0{\cdot}30\\+0{\cdot}21\end{matrix}\right\}$	29·7450 grms.
Empty crucible . . .	27·6429	$\left\{\begin{matrix}-0{\cdot}38\\+0{\cdot}39\end{matrix}\right\}$	27·6426 grms.
Weight of substance			2·1024 grms.

The method of calculating the corrections is as follows:—The 29 grms. is made up from $[20]+[5]+[2]+[1]_a+[1]_b$, which have respectively the correction factors $-0{\cdot}07$, $-0{\cdot}23$, $-0{\cdot}08$, $+0{\cdot}06$, $+0{\cdot}02$. The 0·74 grm. was made up from the $[0{\cdot}5]+[0{\cdot}2]+[0{\cdot}02]+[0{\cdot}01]_a+[0{\cdot}01]_b$ with the tabulated corrections: $+0{\cdot}04$, $+0{\cdot}05$, $+0{\cdot}05$, $+0{\cdot}03$, $+0{\cdot}04 = +0{\cdot}21$. Hence, 29·7459 is to be increased by $-0{\cdot}30+0{\cdot}21$, that is, by $-0{\cdot}09$; etc.

In the course of time the weights gradually decrease in weight. This is due to "wear and tear." Highly polished weights are less liable to loss by wear than weights with a dull surface.[1] The weights—particularly the smallest—sometimes become heavier. This can usually be traced to the adhesion of dirt to the metal. The following example[2] illustrates the effect of wear on a set of weights which had been in regular use for some years in a laboratory where the need for calibrating the weights was considered superfluous:—

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[1] The Berichte der Kaiserlichen Normal-Echungskommission (*Chem. Ztg.*, **10.** 1481, 1886) mentions a change, due to internal oxidation within the blowholes of the castings, which was accelerated by the introduction of salt solutions when the weights were gilded.

[2] H. D. Richmond, *Analyst*, **19.** 99, 1894; B. Weinstein, *Handbuch der physikalischen Maassbestimmungen*, Berlin, **2.** 363, 1888; R. C. Benner, *Mining Sci. Press*, **100.** 492, 1911; T. K. Rose, *The Metallurgy of Gold*, London, 460, 1906.

Table IV.—Effect of Use on a Set of Weights.

Face value.	Actual value.	Face value.	Actual value.	Face value.	Actual value.
$[10]_a$	Standard	$[1]_b$	0·9989	$[0{\cdot}1]_b$	0·0982
$[10]_b$	9·9997	$[1]_c$	1·0008	$[0{\cdot}05]$	0·0485
$[5]$	4·9990	$[0{\cdot}5]$	0·4982	$[0{\cdot}02]$	0·0191
$[2]$	1·9991	$[0{\cdot}2]$	0·1993	$[0{\cdot}01]_a$	0·0092
$[1]_a$	0·9987	$[0{\cdot}1]_a$	0·0971	$[0{\cdot}01]_b$	0·0089

These numbers speak eloquently of the need for checking the weights from time to time. They also show how two analysts might get different results with the same analytical process when possibly one is using faulty weights.[1]

§ 9. The Influence of Inequalities in the Lengths of the Arms of the Balance on the Weighing.

In what precedes, it has been assumed that the two arms of the balance are equal in length. This is not really the case. It is a mechanical impossibility to ensure perfect equality. To find the difference in the lengths of the two arms, add weights of the same nominal value to each pan. The (corrected) weights should be about half the maximum load—say, 50 grms. Bring the balance into equilibrium by means of a rider. Interchange the weights on the pan, and again bring the balance into equilibrium by means of the rider. Call the two weights W and w, and let l and r respectively denote the additional weights required for equilibrium on the left and right sides. Then, on the first weighing,

$$w + l = W\,; \text{ and } W = w + r$$

on the second weighing. Let L and R respectively denote the lengths of the left and right arms. Then, from the law of levers,

$$L(w + l) = R\,.\,W\,; \text{ and } L\,.\,W = R(w + r).$$

Multiply these two expressions together, and reduce by the usual method of approximation for small quantities. We obtain:

$$\frac{R}{L} = 1 + \frac{l - r}{2w}\,; \text{ and } \frac{L}{R} = 1 - \frac{l - r}{2w} \quad . \quad . \quad . \quad (1)$$

Suppose that the weighings with corrected weights for an ordinary analytical balance were found to be:

Left.	Right.
$[50]$	$[20] + [10]_a + [10]_b + [10] + 0{\cdot}13$ mgrm.
$[20] + [10]_a + [10]_b + [10]$	$[50] + 0{\cdot}19$ mgrm.

Here then $l = -0{\cdot}13$, and $r = +0{\cdot}19$ mgrm. Consequently, from the second equation, (1), above,

$$L : R = 1 : 1{\cdot}0000032.$$

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[1] The consistency of the riders can easily be checked from the 0·01-grm. weights, or a standard rider. In the above case the adjustment of the rider has been effected in terms of the given rider. T. K. Rose (*l.c.*) reports that he found some gilded brass riders at the Royal Mint increased in weight from 5·0 to 5·025 mgrms. in six months.

It is then necessary to find the magnitude of the error introduced in a weighing for a known deviation from equality in the lengths of the two arms of the balance. The inequality may be allowed for by multiplying the *apparent weight* by the ratio of the lengths of the two arms; using the ratio $R : L$ or $L : R$ according to the arm with which the weight is connected. This is necessary if the true weight of the object is to be determined.

With the preceding ratio, $L : R = 1{\cdot}0000032$, a weight w on the left pan will be equivalent to a weight $w \times 1{\cdot}0000032$ on the right pan. Hence, if a substance on the left pan balances the weight $50 + 0{\cdot}0001$ grm. on the right pan, the weight of the load is $w = 1{\cdot}0000032 \times 50{\cdot}0001 = 50{\cdot}0016$ grm.—an error of about 0·003 per cent. There is therefore no need to apply the correction. Each balance has its own constant $R : L$ for a given load. The numerical value of the ratio varies with different loads.

Most analytical balances do not need an allowance for variations due to inequalities in the lengths of the arms; the lengths are usually made sufficiently exact. When the weights are always placed, say, in the right pan, the correction need not be applied in analytical work, because, although there may be a difference between the apparent and the true weight of the substances which are weighed with the faulty balance, yet this difference is constant and does not affect the value of the ratio. For instance, if R and L respectively denote the lengths of the right and left arm, and the true weights $w_1, w_2, w_3, \ldots$ are represented on the balance by the apparent weights $p_1, p_2, p_3, \ldots$, it follows, from the law of levers, that $w_1L = p_1R$; $w_2L = p_2R$; . . . Hence,

$$p_1 = \frac{L}{R}w_1; \quad p_2 = \frac{L}{R}w_2; \quad p_3 = \frac{L}{R}w_3; \; \ldots$$

This means that the value of the ratio of the true weights is the same as the value of the ratio of the apparent weights. That is,

$$w_1 : w_2 : w_3 = \frac{L}{R}w_1 : \frac{L}{R}w_2 : \frac{L}{R}w_3 = p_1 : p_2 : p_3.$$

Consequently, when two quantities of matter are increased or decreased in the same proportion,[1] they will equally balance one another. Hence, *if the weights be always confined to one pan, the apparent weights will always be increased or decreased in the same ratio, and the results of an analysis will be as accurate on the defective balance as on a balance with arms perfectly equal.* This method of eliminating the error due to the inequality of the arms of the balance presupposes that no weights are placed on the left pan for the purpose of making up a given weight in what may sometimes appear to be the easiest manner, by subtraction.

§ 10. Corrections for the Buoyancy of Air.

It is assumed that, if two things are equal in weight at the same time and place, they contain the same mass or quantity of matter. The mass of a 100-grm. weight is supposed to be 100 times the mass of a 1-grm. weight. This assumption is only true if the two substances have the same volume, or if the comparison be made *in vacuo*. A body weighed in air is partly buoyed up by a pressure equivalent to the weight of a volume of air equal to the volume of the body (Archimedes' principle). Suppose that a 100-grm. platinum weight (sp. gr. 21·55) be balanced against a 100-grm. brass weight (sp. gr. 8·4). It is easy to show that the weight of dry air at 0° and 760 mm. displaced by the platinum weight is equal to 0·0054 grm.[1]; while the weight of the air displaced by the 100-grm. brass weight is 0·0143 grm. Hence, if the platinum weight be exactly 100 grms., the brass weight which exactly counterpoises it will not be 100 grms., but $100+(0{\cdot}0143-0{\cdot}0054)=100{\cdot}0089$ grms. Hence, *the buoyancy of the air thus produces a sensible effect whenever the volume of the load differs materially from the volume of the weight.*[2]

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[1] It is assumed that the same kind of matter is in question, or that the effect of the buoyancy of the air is eliminated. See R. Kempf, *Chem. Ztg.*, 36. 1349, 1912.

The arithmetic of the above calculation is summarised in the formula:

$$\text{Corrected weight} = w + \omega\left(\frac{w}{s} - \frac{w}{s_1}\right) \quad . \quad . \quad . \quad . \quad (1)$$

where w represents the apparent weight of the object; s, the specific gravity of the object being weighed; s_1, the specific gravity of the weights; and ω, the weight of a cubic centimetre of air at the temperature, pressure, and humidity prevailing at the time of observation.

EXAMPLE.—A porcelain crucible (sp. gr. 2·3) weighs $w=7{\cdot}5392$ grms. when the 7-grm. weights are brass ($s_1=8{\cdot}4$) and the 0·5392-grm. weights are platinum ($s_2=21{\cdot}55$). What is the corrected weight of the body when $\omega=0{\cdot}0012$?

With the 7-grm. brass weights,

$$\text{Correction} = 7 \times 0{\cdot}0012\left(\frac{1}{2{\cdot}3} - \frac{1}{8{\cdot}4}\right) = 0{\cdot}00245 \text{ grm.};$$

and with the 0·5392-grm. platinum weights,

$$\text{Correction} = 0{\cdot}05392 \times 0{\cdot}0012\left(\frac{1}{2{\cdot}3} - \frac{1}{21{\cdot}55}\right) = 0{\cdot}00030 \text{ grm.}$$

Consequently, the corrected weight is $7{\cdot}5392+0{\cdot}0026+0{\cdot}0003=7{\cdot}5421$ grms.

To illustrate the effect of the buoyancy of air on the different precipitates usually weighed in clay analyses, the following table may be quoted:—

Table V.—Effect of Buoyancy of Air on the Weighings of a Clay Analysis.

Substance weighed.	Specific gravity.	Error per gram of substance weighed.	
		Brass weights.	Platinum weights.
Clay	2·55	0·00033	0·00041
Silica	2·23	0·00039	0·00048
Alumina	3·85	0·00017	0·00028
Ferric oxide	5·12	0·00010	0·00018
Magnesium pyrophosphate	2·40	0·00036	0·00044
Calcium oxide	2·90	0·00027	0·00035
Potassium chloride	1·99	0·00046	0·00065
Sodium chloride	2·13	0·00042	0·00054
Potassium chloroplatinate	3·34	0·00021	0·00027

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[1] Thus, the 100-grm. platinum weight has a volume $100 \div 21{\cdot}55 = 4{\cdot}5$. One c.c. of air weighs 0·0012. Hence $0{\cdot}0012 \times 4{\cdot}5 = 0{\cdot}0054$ grm. Of course, we ought to take the weight *in vacuo*, but the error introduced by taking the apparent weight in air is negligibly small. If the correction be 0·001 grm., the error only amounts to 0·000001 grm.

[2] The buoyancy correction appears to have been first used by E. Turner about 1830 in determinations of specific gravities and atomic weights (*Phil. Trans.*, **119**. 291, 1829; **123**. 523, 1833). J. J. Berzelius used the correction in some early work, but later regarded the correction as trifling. W. Crookes, *Chem. News*, **15**. 191, 1867; **29**. 29, 1874; C. W. Folkard, *ib.*, **29**. 30, 1874; F. C. Cloud, *ib.*, **35**. 133, 1874; H. R. Proctor, *ib.*, **30**, 255, 1874; *Trans. Newcastle Chem. Soc.*, **2**. 188, 1873; L. L. de Koninck, *Chem. Ztg.*, **18**. 1816, 1894; J. P. Cooke, *Zeit. anal. Chem.*, **23**. 187, 1884; *Chem. News*, **48**. 39, 1883; W. H. Miller, *Phil. Trans.*, **146**. 753, 1856; G. F. Becker, *Liebig's Ann.*, **195**. 222, 1879. To eliminate the buoyancy correction in weighing bulky glass apparatus use a similar apparatus as a tare—see page 550.

The table shows that when the amount of a precipitate is determined from the difference in the weight of an empty crucible and of the crucible plus residue, and the atmospheric conditions are the same when the two weighings are made, the buoyancy correction is not needed for small precipitates, nor for precipitates with a specific gravity not sensibly different from that of the substance undergoing analysis. In ordinary analytical operations we have to deal with *differences* in weight, not with absolute weights. For instance, an empty platinum dish weighs 63 grms. It is weighed with brass weights (sp. gr. 8·4). A litre of water is evaporated to dryness in the dish, and the dish weighed again. The difference in the two weighings represents the solid matter derived from the water.

If there be a considerable difference between the specific gravity of the substance undergoing analysis and the weight of the ignited precipitate, an allowance must sometimes be made for the different effects of the buoyancy of the air on the different substances. For instance, in determining the amount of sulphur in a sample of pyrites by weighing the precipitated barium sulphate, the error due to the buoyancy of air will be negligibly small. This arises from the fact that the pyrites and the barium sulphate have nearly the same specific gravity, and, consequently, nearly the same buoyancy correction. On the contrary, in standardising a solution of silver nitrate by precipitating silver chloride from a given volume of the solution, the buoyancy of air may affect the result by $\frac{1}{10}$th per cent.

Effect of Variations of Temperature and Pressure on the Buoyancy of Air.—In the experiment cited above, we assumed that the weight of the empty platinum dish was affected by the air to the same extent before and after the evaporation. It is necessary to examine the validity of this hypothesis. The evaporation takes so long that we cannot reasonably assume that the temperature and barometric pressure have remained constant. The weight of a given volume of air, of course, depends upon the temperature and pressure. Hence the buoyancy of the air is affected by these two factors.

The brass weights, 63 grms. in the above example, occupy a volume of 7·5 c.c., and the material of the platinum dish occupies a volume of 2·99 c.c. Hence, 7·5 – 2·92 = 4·58 c.c. more air is buoying up the brass than the platinum weights. The weight of 4·5 c.c. of air at 760 mm. and 15° is 4·58 × 0·001227 = 0·00552 grm. Consequently, the 63-grm. brass weights really represent 63·00552 grms. Suppose that the barometer falls to 740 mm. and the temperature rises to 25°, the weight of the 4·5 c.c. of air[1] will then be 4·5 × 0·001173 = 0·00528 grm. Hence, 0·00552 – 0·00528 = 0·00024 grm. represents the decreased buoyancy of air during the second weighing. Hence, if the dish weighed just 63 grms. the first weighing, it would weigh 63·00024 grms. the second weighing.

Assuming the two atmospheric conditions just indicated, and assuming that the observed weights were:

Dish plus residue	63·00048 grms.
Empty dish	63·00000 grms.
Residue	0·00048 grm.

we might be led to assume that the litre of water contained the equivalent of 0·00048 grm. of solid matter, when in reality it only contained 0·00024 grm. The apparent weight of the dish has increased 0·00024 grm. owing to the decreased

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[1] The weight in grams of a litre of dry air at any temperature and pressure is readily computed by dividing the pressure expressed in mm. of mercury by 273 added to the temperature in ° C. and multiplying the quotient by 0·4644. The arithmetic is summarised in the formula:

$$\text{Density of dry air at } t^\circ \text{ and } p \text{ mm. pressure} = \frac{0{\cdot}001293}{1 + 0{\cdot}00367t} \cdot \frac{p}{760}.$$

The product of the volume of the substance and the weight of 1 c.c. of dry air represents the weight of a volume of dry air equal to the volume of the substance.

buoyancy of the air. If, therefore, we make any pretence to accuracy in the fourth place, we must not only allow for the buoyancy of the air, but we must also allow for the changes in the buoyancy of the air with variations of temperature and pressure.[1] Potash bulbs and calcium chloride tubes, in virtue of their relatively large bulk, might easily lead to errors of 1 per cent., owing to the neglect of the variations in the buoyancy of air under changing atmospheric conditions.

Fresenius, in his classical *Anleitung zur quantitativen chemischen Analyse*, after showing[2] that in analytical work weighings are usually carried to the $\frac{1}{10}$th mgrm., refers to the correction for the buoyancy of air in these terms: "This defect is so very insignificant, owing to the trifling specific gravity of air in proportion to that of the solid substance, that we generally disregard it altogether in analytical experiments." Fresenius' remark is also true of analytical practice at the present day, and it is equally true that weighings below 0·0005 grm. are then of no particular value, and this altogether apart from the inaccuracies mentioned on page 15 arising from the particular character of the analytical process.

Effect of Variations of Humidity on the Buoyancy of the Air.—The humidity of the air is also constantly changing. We must therefore inquire what effect this has on the buoyancy of the air.[3] The preceding calculations were referred to *dry* air at the temperatures and pressures indicated. As a matter of fact, the buoyancy of moist air is less than that of dry air; hence, the correction for moist air will be less than for dry air. In illustration,[4] a crucible kept in the balance case during the summer months—July and August—showed the following variations in weight:—

Table VI.—Effect of Humidity of Air on Weighings.

	Weight in air.	Weight corrected for the buoyancy of dry air.	Weight corrected for buoyancy of moist air.
	grms.	grms.	grms.
Maximum	39·35659	39·37046	39·37061
Minimum	39·35601	39·37040	39·37052
Mean	39·356362	39·370437	39·370562
Deviations from mean	+0·000228 −0·000352	+0·000023 −0·000037	+0·000048 −0·000042

Hence, the average effect of variations in moisture is somewhere near 0·00013 grm. In one of the experiments, a variation of 10 per cent. in the humidity of the air only altered the corrected weight 0·00003 grm. That is outside the range of weighings conducted to $\frac{1}{10}$th milligram. Applying our test—the errors in weighing should fall within the limits of experimental error due to the analytical process—it follows that it is necessary to allow for variations in the buoyancy of air due to variations of temperature and pressure when the weighings are conducted to the $\frac{1}{10}$th of a milligram, but further variations due to humidity can be neglected under these conditions.

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[1] THE EFFECT OF GRAVITATION ON THE BUOYANCY OF AIR.—Strictly speaking, the weight of a litre of dry air at 760 mm. differs in different localities. This is not merely because the action of gravity on a litre of air is different in different places, but because a pressure of 760 mm. of mercury varies with the intensity of gravitation. Thus, the intensity of gravity at Greenwich is to that at Paris as 3457 : 3456. Hence, if a litre of dry air at Paris weighs 1·2932 grms., a litre of air at Greenwich will weigh 1·2936 grms. under the same conditions of pressure and temperature. Hence, the effect of gravitation on the buoyancy correction is negligible. The small difference in the buoyancy of air in the two places has no appreciable effect when applied to particular cases.

[2] R. Fresenius, *Quantitative Chemical Analysis*, London, I. 18, 19, 1876.

[3] The fallacy of assuming that the air inside a balance case is dry simply because a couple of jars of calcium chloride or of sulphuric acid are in the case will appear from page 10.

[4] O. Kuhn, *Chem. Ztg.*, 34. 1097, 1108, 1910; R. Kempf, *ib.*, 36. 1349, 1912.

It is generally convenient to assume that the average weight of a cubic centimetre of moist air is 0·0012 grm.[1] Remembering that for general purposes

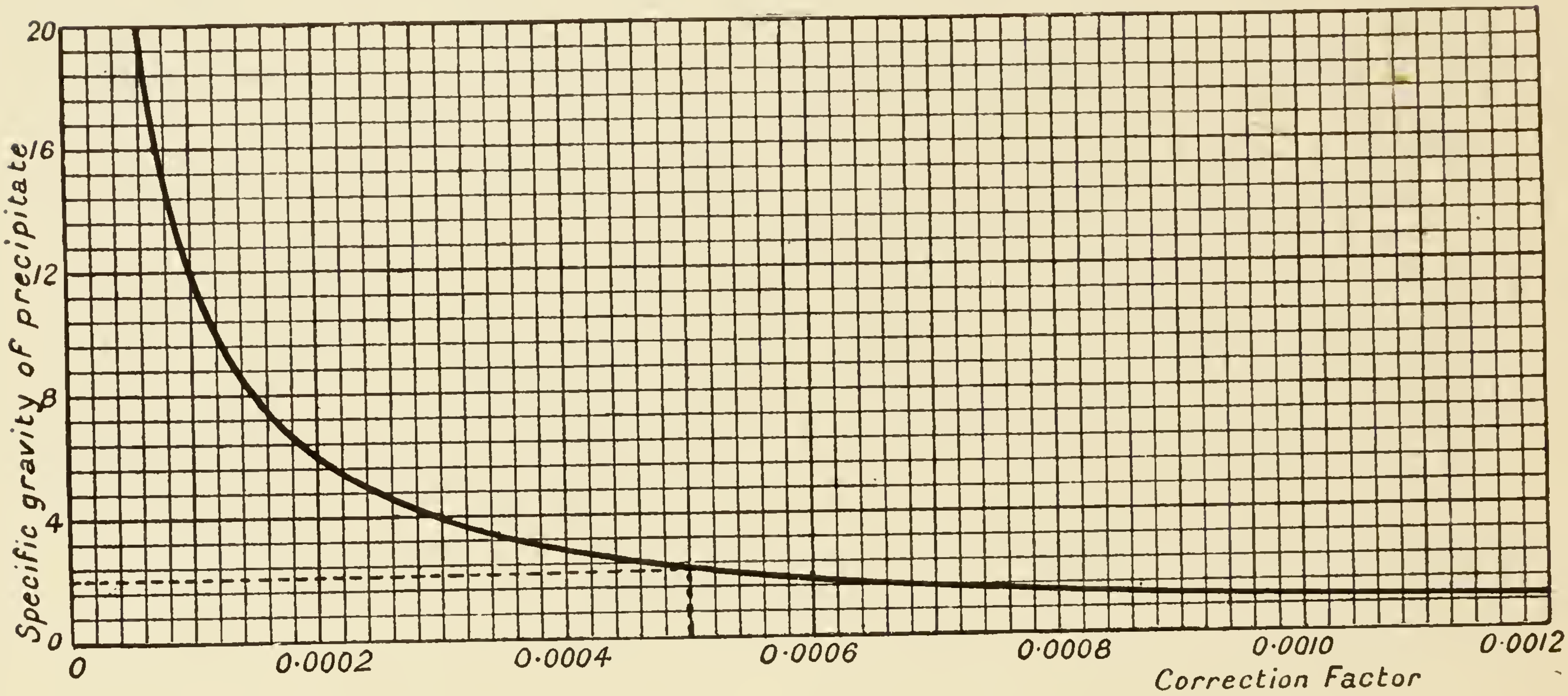

FIG. 8.—Buoyancy correction for substances of different specific gravity.

the weights are calibrated in air, and that we assume the buoyancy is a constant corresponding with the weight 0·0012 grm. per c.c., we are only concerned with variations in the buoyancy of the object being weighed.[2] In that case, we use, in place of (1),

$$\text{Corrected weight} = w + 0{\cdot}0012\frac{w}{s} \quad . \quad . \quad . \quad . \quad (2)$$

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[1] If f denotes the actual pressure (in mm. mercury) of the vapour present in a unit volume of moist air (saturated or unsaturated), the weight of the moist air is determined from the formula page 24 by substituting $p - \frac{3}{8}f$ in place of the barometric pressure p. We thus obtain:

$$\text{Density of moist air at } t^\circ \text{ and } p \text{ mm. pressure} = \frac{0{\cdot}001293}{1 + 0{\cdot}00367t} \cdot \frac{p - \frac{3}{8}f}{760}.$$

Remember that the mass of vapour present in a given volume of moist air saturated at a given temperature depends upon the temperature, and is independent of the pressure; and that the pressure of water vapour at the dew-point is nearly the same as the pressure f at the given temperature. The value of f is the maximum pressure of the water vapour at the dew-point, and this can be obtained from a table of the vapour pressures of water at different temperatures (Table LXXXV.). Hence, the relative humidity of air is the ratio of the maximum pressure of the aqueous vapour, f, at the dew-point, to the maximum pressure, F, at the actual temperature of the air; or

$$\text{Relative humidity} = \frac{f}{\mathrm{F}}.$$

EXAMPLES.—(1) What is the relative humidity of air at 15° when the dew-point is 10°? From Table LXXXV., the maximum pressures of the aqueous vapour at these two temperatures are respectively 12·79 and 9·21. Hence, $9{\cdot}21 \div 12{\cdot}79 = 0{\cdot}72$, or 72 per cent. humidity.

(2) What is the density (or the weight of 1 c.c.) of moist air at 15° when the dew-point is 10°, and the barometer 759·14 mm.? From Table LXXXV., the maximum pressure of water vapour at 10° is 9·21 mm. Hence, by substituting $f = 9{\cdot}21$, $t = 15^\circ$, and $p = 759{\cdot}14$ in the above formula, it follows that 1 c.c. of moist air at 15° weighs 0·001219 grm.

[2] W. Dittmar, *Exercises in Quantitative Chemical Analysis*, Glasgow, 8, 1887; P. Schottländer, *Zeit. phys. Chem.*, **16**. 458, 1895.

By making $w = 1$ grm. and plotting the corrected weight for different values of s (specific gravity), we get the curve shown in fig. 8. This enables the correction for a given weight of substance to be seen at a glance.

EXAMPLE.—A silica "precipitate" weights 0·6021 grm. What is the corrected weight if the specific gravity of calcined silica is 2·25 ? From the diagram (dotted lines), we see that the correction factor is 1·0005 per grm. Hence, $1{\cdot}0005 \times 0{\cdot}6021 = 0{\cdot}6024$ grm. is the corrected weight.

§ 11. Summary.

The important lesson we learn from this chapter is that in analytical chemistry, as well as in other work involving delicate measurements, it is always advisable to make, at least, a rough estimate of the influence of the various sources of error on the final result. These errors can only be neglected when their effect is small in comparison with the error derived from other sources. The chief sources of error commonly introduced in the balance room are those arising from: (1) Variations in the zero point of the balance; (2) Inconsistent weights; (3) Inequalities in the lengths of the arms of the balance; and (4) The buoyancy of the air. We have seen that in weighings making any pretence to accuracy to the "second decimal" or to the "$\frac{1}{10}$th milligram"—

(1) The zero point of the unloaded balance should be determined and the weighing made by the method indicated in the text[1] (pages 10 to 13).

(2) The weights should be calibrated, and periodically checked (pages 16 to 21) for consistency amongst themselves.

(3) The error due to the inequality in the arms of the balance can be neglected in ordinary analytical work (page 21).

(4) The correction of the weighings for the buoyancy of air is necessary when the determination involves the weighing of substances with appreciably different specific gravities (page 23). In general analytical work this correction can be neglected, since the resulting error is overshadowed by the errors associated with the preparation of the precipitates for the balance.

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[1] Or, of course, some of the other methods indicated by name on page 11.

CHAPTER II.

THE MEASUREMENT OF VOLUMES.

§ 12. Volumetric and Gravimetric Processes of Analysis.

Measurements with a good balance and weights can readily be conducted with a precision far greater than is needed for general analytical work. It has been pointed out that the errors involved in the preparation of a troublesome precipitate for weighing will impair the value of an exact weighing. The measurement of volume, in volumetric analysis, may not be so precise and reliable as the measurement of weight, yet the results of volumetric processes, based on suitable reactions, are frequently more trustworthy than gravimetric processes, because the method of preparing the substance for the measurement by volumetric processes is less liable to error.

There is a prejudice in some minds against volumetric processes. It is claimed that in general "there is a lack of precision in volumetric analysis." In many cases the prejudice arises from the fact that some essential precautions have been neglected; in other cases there may be an intrinsic weakness in the method itself. There is also some confusion possible in the different systems of measurement. With proper precautions many volumetric processes are excellent, and, for technical analyses, invaluable. Indeed, in technical work, where time is an essential factor, volumetric processes are used in preference to gravimetric wherever expedient.[1] It is important to have a clear idea of the precautions necessary for a high degree of accuracy, in order that errors of vital importance may be eliminated. The need for the "analytical perspective," mentioned on page 16, is here of great moment.

§ 13. The Influence of Variations of Temperature.

The volume of a solution depends on the temperature. The higher the temperature, the greater the volume of a given weight of a solution. A glass measuring vessel also has a greater capacity the higher the temperature. Although the level of a solution in, say, a litre flask may rise above the litre mark as the temperature rises, this naturally occurs because the expansion of the water more than counterbalances the increased capacity of the flask. If the expansion of the glass were greater than the expansion of the solution, with rise of temperature, the level of the liquid in a standard flask would sink below the mark on the neck of the flask.[2] The liquid would appear to contract. The volume measured at any temperature, different from the standard temperature, is the joint effect of the changed capacity of the flask and the changed volume of the liquid.

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[1] R. Hasenclever, *Ber.*, 33. 3827, 1900.

[2] Text-books on Heat describe experiments illustrating this point.

Let us take the coefficient of cubical expansion of glass[1] to be 0·000025; and Thiesen, Scheel, and Disselhorst's[2] values for the volume of water at different temperatures indicated in the subjoined table (Table VII.). The number of cubic centimetres of water which must be subtracted from or added to 1000 c.c. of water to give the volume of distilled water at $t°$, in order to fill a litre flask calibrated at 15°, is indicated in the following table[3] (Table VIII.). The data have been calculated from the preceding Table VII.[4]

Table VII.—Volume and Density of Water at Different Temperatures.

Temp.	Volume.	Density.	Temp.	Volume.	Density.
0	1·0001324	0·9998676	20	1·0017728	0·9982303
1	1·0000734	0·9999266	21	1·0019853	0·9980186
2	1·0000320	0·9999680	22	1·0022083	0·9977966
3	1·0000078	0·9999922	23	1·0024414	0·9975645
4	1·0000000	1·0000000	24	1·0026847	0·9973225
5	1·0000082	0·9999918	25	1·0029378	0·9970708
6	1·0000320	0·9999680	26	1·0032006	0·9968097
7	1·0000707	0·9999293	27	1·0034729	0·9965391
8	1·0001241	0·9998759	28	1·0037546	0·9962594
9	1·0001917	0·9998084	29	1·0040455	0·9959708
10	1·0002730	0·9997271	30	1·0043456	0·9956732
11	1·0003678	0·9996324	31	1·0046546	0·9953670
12	1·0004756	0·9995246	32	1·0049724	0·9950522
13	1·0005962	0·9994041	33	1·0052989	0·9947290
14	1·0007292	0·9992713	34	1·0056341	0·9943975
15	1·0008744	0·9991264	35	1·0059777	0·9940578
16	1·0010314	0·9989697	36	1·0063297	0·9937101
17	1·0012000	0·9988014	37	1·0066899	0·9933545
18	1·0013799	0·9986220	38	1·0070584	0·9929911
19	1·0015709	0·9984315	39	1·0074349	0·9926200

Table VIII.—Reduction for the Change of the Apparent Volume of a Litre of Water with Temperature. (Standard temperature = 15°.)

Temp.	0	1	2	3	4	5	6	7	8	9
0	...	...	...	...	...	+0·63	+0·62	+0·60	+0·57	+0·53
1	+0·48	+0·41	+0·32	+0·22	+0·12	Unit.	−0·13	−0·28	−0·43	−0·60
2	−0·77	−0·96	−1·16	−1·37	−1·58	−1·81	−2·05	−2·30	−2·57	−2·82
3	−3·10	−3·38	−3·67	−3·97	−4·28	−4·60	−4·93	−5·27	−5·61	−5·96

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[1] The value for glass used in volumetric work ranges from 0·000023 to 0·000028, according to the nature of the glass. The error introduced by these variations is negligibly small.

[2] M. Thiesen, K. Scheel, H. Disselhorst, *Wiss. Abh. phys. tech. Reich.*, **3**. 1, 1901.

[3] For a table based upon some older data, see P. Casamajor, *Journ. Amer. Chem. Soc.*, **1**. 188, 1876; **2**. 19, 1877; *Chem. News*, **35**. 160, 170, 1877; **38**. 137, 1879. See also W. Schlösser, *Zeit. angew. Chem.*, **17**. 953, 977, 1004, 1904; **21**. 2161, 1908; *Chem. Ztg.*, **29**. 509, 1904; *Zeit. anal. Chem.*, **46**. 392, 1907; H. L. Payne, *Journ. Anal. App. Chem.*, **6**. 326, 1892.

[4] If a "temperature of reference" other than 15° be adopted, another table can be easily compiled from this. For instance, suppose 20° be adopted, 15° becomes +0·77°, 25° becomes −1·04°, etc.

The use of Table VIII. may be illustrated by the following examples:—

EXAMPLES.—(1) 25 c.c. of water are measured in a burette at 28°: what is this volume at the standard temperature, 15°? From Table VIII. it follows that since 1000 c.c. requires a correction of $-2{\cdot}57$ at 28°, 25 c.c. will require a correction of $-0{\cdot}06$. Hence, $25-0{\cdot}06=24{\cdot}94$ c.c. is the required volume.

(2) What is the volume at 15° of a litre of water measured in a flask at 10°, and also at 18°? From the table, the correction for 1000 c.c. at 10° is $+0{\cdot}48$, and at 19°, $-0{\cdot}43$. Hence the required volumes are $1000+0{\cdot}48=1000{\cdot}48$ c.c. at 15°, and $1000-0{\cdot}43=999{\cdot}57$ c.c. at 18°.

Table VIII. thus represents the volume which a litre of water alters in a glass vessel when its temperature changes from the standard 15°. If the prevailing temperature does not differ by more than, say, 3° from the standard 15°, the changes may be ignored. These numbers differ so little from the results with $\frac{1}{5}$N- and $\frac{1}{10}$N-solutions that they may be also used for such solutions. Normal and still more concentrated solutions require special tables, since the deviations are then greater—see, for example, Tables XIII. and XXXV.

In weighing a litre of water in a glass vessel, the most important source of error arises from the variation of temperature. A difference of 1° will give a difference of 0·02 c.c., corresponding with 0·002 per cent. A variation of the barometer of 15 mm. of mercury will cause an error of two units in the second significant figure, and this will affect the measurement by 0·014 c.c. Hence, barometer variations can generally be neglected.

In titrating hot liquids, there is a danger of heating the burette and its contents. In such cases, burettes with a delivery jet at the side (fig. 9) are recommended. Koninck's burette[1] is an ordinary burette with a ┌─'-shaped jet. The idea is to prevent clouding the burette with condensed steam, and the heating of the liquid in the burette, which would cause an expansion of the contained solution.

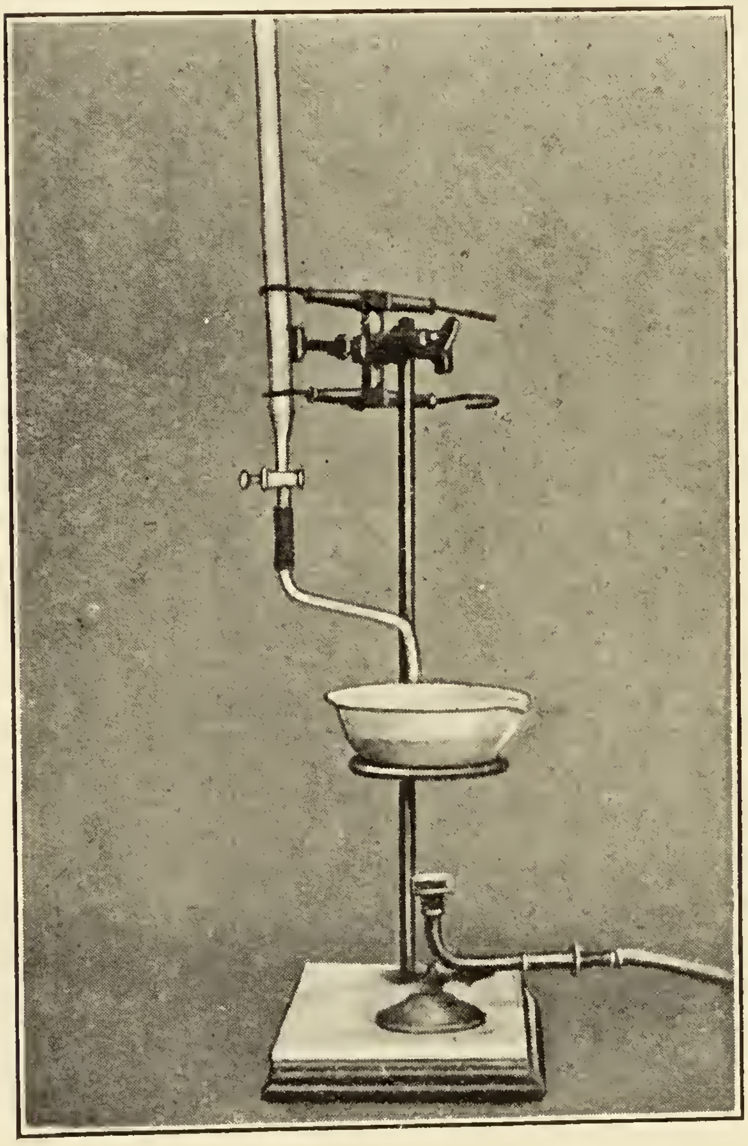

FIG. 9.—L. L. de Koninck's burette.

§ 14. The Litre and its Subdivisions.

Owing to the great difficulty in measuring directly the relation between cubic capacity and the unit of length, the International Committee of Weights and Measures,[2] in 1880, recommended that the word "litre" be used to represent "the volume of a kilogram of pure water at its maximum density"; and in 1901 this definition was amplified to read: "The litre is the volume occupied by the mass of one kilogram of pure water at its maximum density and under normal atmospheric pressure."[1] The litre so defined is a little larger—about 50 c.mm.—than a cubic decimetre. Evidently, then, the cubic centimetre is not really the thousandth part of a litre, but a little smaller than the thousandth part. Hence, if it be desirable to distinguish between a "millilitre" and a "cubic centimetre," it would be necessary to abandon the latter term in analytical chemistry, where the unit of volume is based on the definition indicated above.[2]

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[1] L. L. de Koninck, *Zeit. angew. Chem.*, **1.** 187, 1888.

[2] *Procès-Verbaux Comité Internat. Poids et Mesures*, 30, 1880; 175, 1901; P. Chappius, *ib.*, (2), **2.** 72, 1903; J. M. de Lepinay, *Journ. Phys.*, (3), **5.** 477, 1897; D. Mendeléeff, *Proc. Roy. Soc.*, **59.** 143, 1895; W. Schlösser, *Zeit. angew. Chem.*, **16.** 960, 1903.

Unfortunately, there are a number of different litres used in laboratories. The more important are the following:—

(1) *Normal litre.*—The volume of 1000 grms. of air-free water (weighed *in vacuo*) at +4°. If, therefore, the litre flask is marked correctly at +15°, this means that at a temperature of 15° the capacity of the flask is the same as the volume of a kilogram of water at +4°. This is the normal, true, or international litre, used in this work.[3]

(2) *Mohr's litre.*—The flask contains the same number of grams of water (free from air) at the specified temperature as the number of cubic centimetres or grams stated on the flask. For instance, the Mohr's litre is "the volume occupied by a kilogram of water, at 17·5°, when weighed in air with brass weights."[4]

It matters very little, in analytical work, which litre be adopted, but it is necessary to keep rigorously consistent to the one system in all volumetric apparatus—burettes, pipettes, etc. This matter is serious enough to require emphasis, since apparatus, if not specifically ordered, may be supplied by the dealers, at different times, graduated according to different systems, and mixed graduations may thus be introduced on one bench. We can get some idea of the magnitude of the error which would be introduced in confusing the different systems, by noting that the two "litres" indicated above are related as (1) 1000; (2) 1002·3 c.c. Hence the normal litre is to the Mohr's litre[5] as 1 : 1·0023.

Standard Temperature.—It would be exceedingly inconvenient, if not impossible, to weigh exactly a kilogram of water at +4° *in vacuo*; nor is it practicable to work at +4°. Some other more convenient temperature must be selected, and the necessary corrections made. In this work, 15° is supposed to be the standard temperature.[6] This temperature is recommended by the Kaiserliche Normal-Echungskommission (K.N.E.K.),[7] Berlin; 17·5° was recommended by Mohr,[8] and by Treadwell; 18°, by Lundén;[9] and 20° is recommended by Wagner,[1] and the U.S. Testing Laboratory.[2] The right choice should be determined by the prevailing temperature of the laboratory. Apparatus intended for working in warm climates may be graduated for 20°, 22°, or 25°; and 15° or 17·5° for cooler climes.

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[1] The temperature of maximum density is not defined—it appears to be a shade under 4° C.—nor does the definition make any reference to weighing *in vacuo*. In the calculations it is assumed the weighings are *in vacuo*.

[2] T. W. Richards, *Journ. Amer. Chem. Soc.*, **26**. 413, 1904.

[3] At 15°, therefore, this litre does not represent 1000 grms. of water, but rather 998·069 grms.

[4] F. Mohr, *Zeit. anal. Chem.*, **7**. 285, 1868; H. Beckurts, *Die Methoden der Massanalyse*, Braunschweig, 42, 1910. Mohr made no allowance for variations in the atmospheric conditions.

[5] First show (page 23) that 1000 grms. of water weighed in air with brass weights at 17·5° are equivalent to 1001·1 grms. if weighed *in vacuo*. Then, since the density of water at 17·5° is 0·99875 (Table VII.), it follows that 998·75 grms. of water at 17·5° will represent a normal litre at 17·5°, for it will occupy the same volume as 1000 grms. of water at 4°. Hence, if 998·75 grms. represent 1000 normal c.c., 1001·1 grms. will represent 1002·3 normal c c.

[6] The tables can, of course, be modified for other appreciably different climates. If the flasks, etc., were cooled for weighing, there would be a danger of the deposition of moisture on their surface.

[7] *Zeit. angew. Chem.*, **6**. 557, 1893; L. A. Fischer, *Journ. Amer. Chem. Soc.*, **20**. 912, 1898; C. Laurent, *Bull. Soc. Chim. Nord France*, **1**. 20, 1891; H. Ost, *Chem. Ztg.*, **14**. 1747, 1899; W. Fresenius, *Zeit. anal. Chem.*, **30**. 461, 1891; A. Classen, *Theorie und Praxis der Massanalyse*, Leipzig, 64, 1912.

[8] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethoden*, Braunschweig (H. Beckurts' edition), 42, 1910; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 432, 1911.

[9] H. Lundén, *Svensk Kem. Tids.*, **24**. 96, 1912.

From the discussion on page 31 it is easy to find what amount of water must be weighed at any given temperature to have a volume equal to the volume of a kilogram of water at +4°. Given the specific gravity of air, say, 0·0012 kilogram per litre; the specific gravity of the brass weights, 8·4; the coefficient of cubical expansion of glass, 0·000025. Let S denote the specific gravity of water at $t°$—Table VII. *To find what amount of water at any specified temperature must be weighed in air with brass weights to give a normal litre.* Since a kilogram of water at +4° weighed *in vacuo* occupies 1 litre, it follows from the discussion on page 22 that a litre of water will weigh

$$w = S - 0{\cdot}0012\left(1 - \frac{S}{8{\cdot}4}\right)\text{ kilogram} \quad . \quad . \quad . \quad . \quad (1)$$

when weighed in air with brass weights. But a flask exactly 1 litre at 15° has a capacity of $1 + 0{\cdot}000025(t - 15)$ at $t°$. Hence, it is necessary to weigh

$$W = [1 + 0{\cdot}000025(t - 15)]\left[S - 0{\cdot}0012\left(1 - \frac{S}{8{\cdot}4}\right)\right]\text{ kilogram} \quad . \quad (2)$$

at $t°$ in order to find what the capacity of the flask would be if the water had been weighed *in vacuo* at 4° with brass weights.

Example.—What amount of water must be weighed in a flask at 15° in order that a mark can be made on the neck of the flask to represent the volume of a kilogram of water weighed at 4° *in vacuo*? From Table VII., page 29, $S = 0{\cdot}999126$, and $t = 15$. Substitute these numbers in the preceding formula (2). We get a weight 0·99806 kilograms. In practice, therefore, the flask is counterpoised on the balance, a kilogram weight is placed on the right pan, and $1000 - 998{\cdot}069 = 1{\cdot}931$ grms. on the left pan. When the flask has sufficient water to restore equilibrium, the volume of the water in the flask represents the volume of a kilogram of water at 4° when weighed *in vacuo*.

In order to avoid the labour of calculation, Schlösser[3] has computed a table of values ranging from 5° to 30·9°, referred to air and water at 15°, and the barometer at 760 mm.

§ 15. Meniscus, Parallax Errors, and Burette Floats.

Parallax Errors.—In reading the level of liquids in burettes, pipettes, etc., the lower boundary of the dark meniscus is taken as the normal reading. Parallax errors must be carefully watched. If the eye be not in the same horizontal plane as the meniscus, BB' (fig. 10), the reading may be either too high or too low. For instance, if the eye be looking in the direction AA' the reading will be too high; and if in the direction CC', the reading will be too low. The direction BB' gives a correct reading free from parallax. In the diagram, the correct reading is 30·0 c.c; the two readings affected by parallax errors are AA', 30·3 c.c., and CC', 29·85 c.c. If the mark to be read encircled the burette, the eye would see only one horizontal line when at the proper level for reading. The marks rarely encircle the burette, and some auxiliary is therefore needed.[4]

Meniscus Screens.—The level of the meniscus is rendered more distinct by placing the burette so that it has a white wall as background and shading the light from below by holding two fingers behind the burette just below the meniscus,[1] or Mohr's simple and effective plan of holding a piece of paper, partly blackened, with the blackened portion just below the meniscus, as illustrated in fig. 11.[2]

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[1] J. Wagner, *Zeit. phys. Chem.*, **28.** 193, 1899.

[2] *Circular Bureau of Standards*, **9.** 2, 1904; N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, **4.** 553, 1908.

[3] W. Schlösser, *Zeit. angew. Chem.*, **16.** 960, 1903; *Chem. Ztg.*, **27.** 4, 1904.

[4] A reading lens is often a great help in exact work.

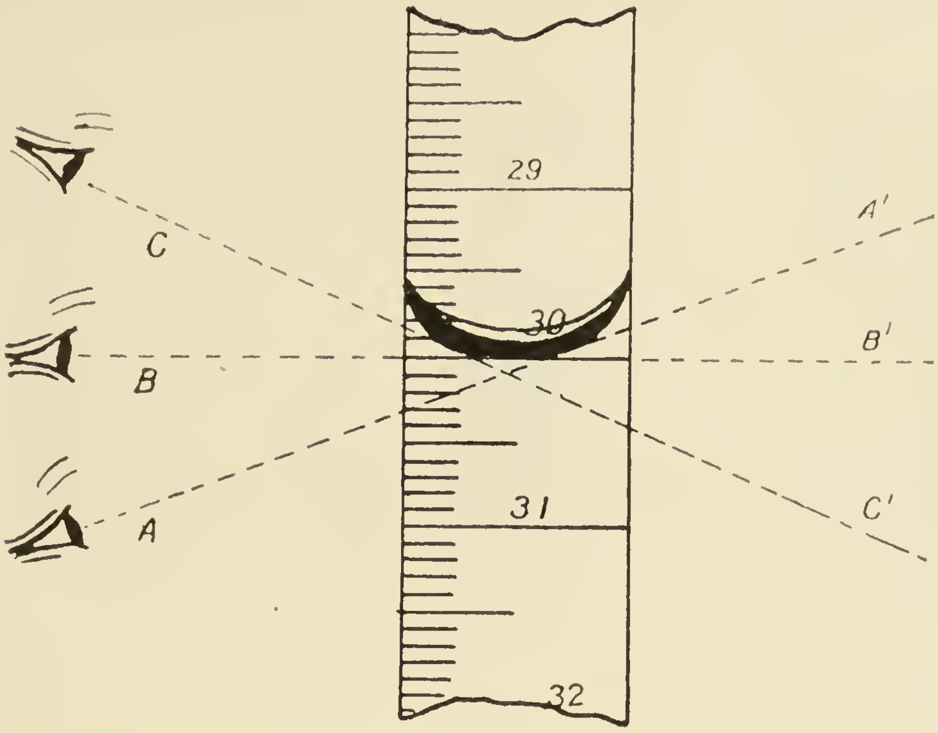

FIG. 10.—Meniscus errors.

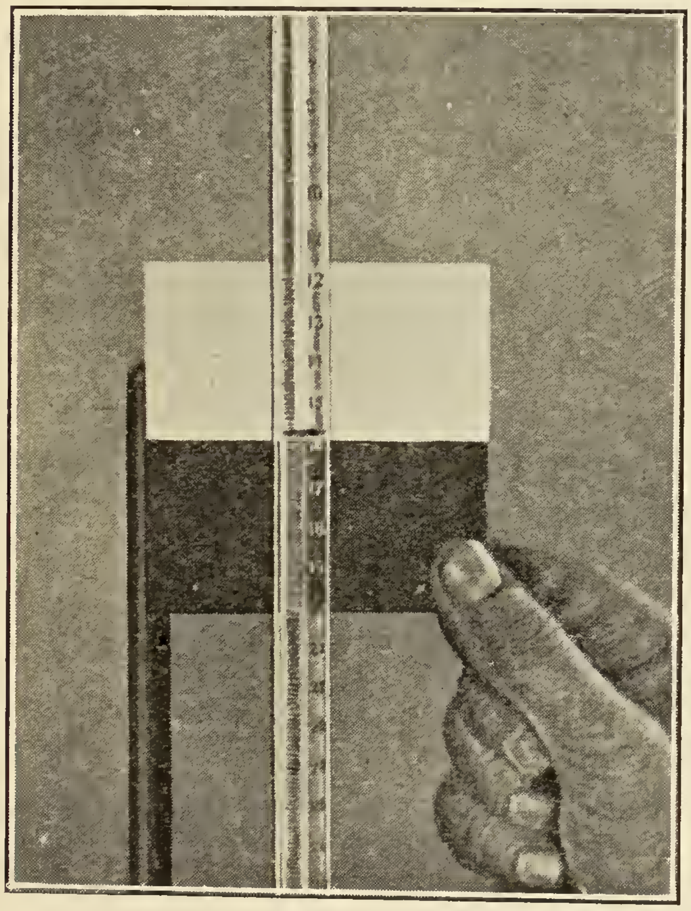

FIG. 11.—Mohr's shaded screen.

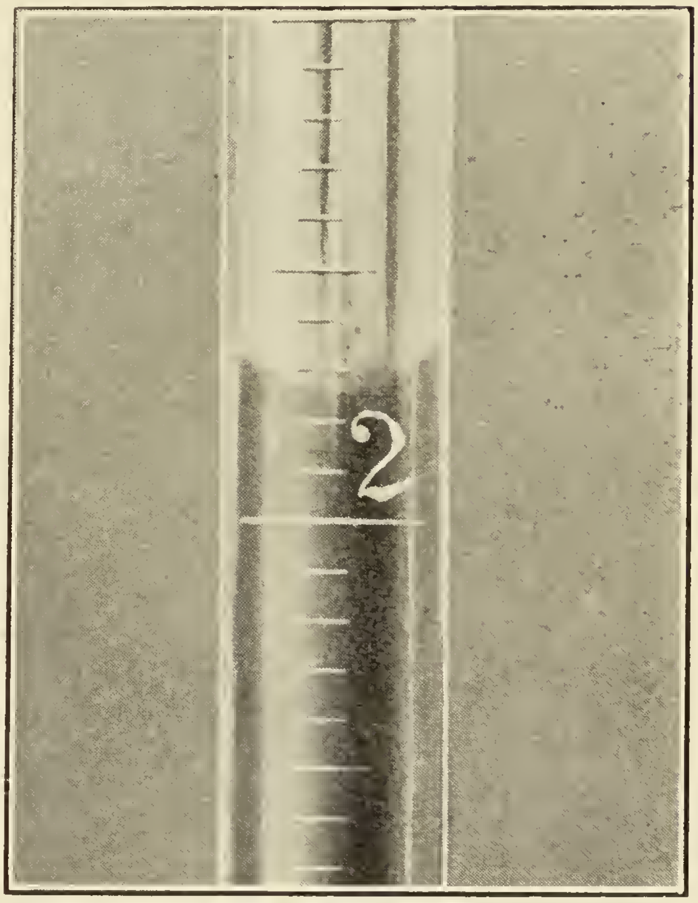

FIG. 12.—Rohrbeck's burette.

Burettes made to Accentuate the Meniscus.—Rohrbeck's burettes (fig. 12), made with a flat instead of a cylindrical tube, make errors due to parallax less likely. The meniscus with these burettes comes out very clearly. Schellbach[1] recommends the use of burettes with two narrow white enamel longitudinal strips separated by a dark-coloured (blue) strip down the back of the burette. A fine point appears symmetrically placed between the strips, and at the boundary of the meniscus (fig. 13)[2] when the eye is in the right position for a reading. If the eye be too high or too low, the point does not appear sharp, but is more or less ill-defined and blunted. A few minutes' trial will soon show that there is a fairly wide range of height and depth within which the point would be adjudged correct for a reading. In spite of this, these burettes are much used.[3]

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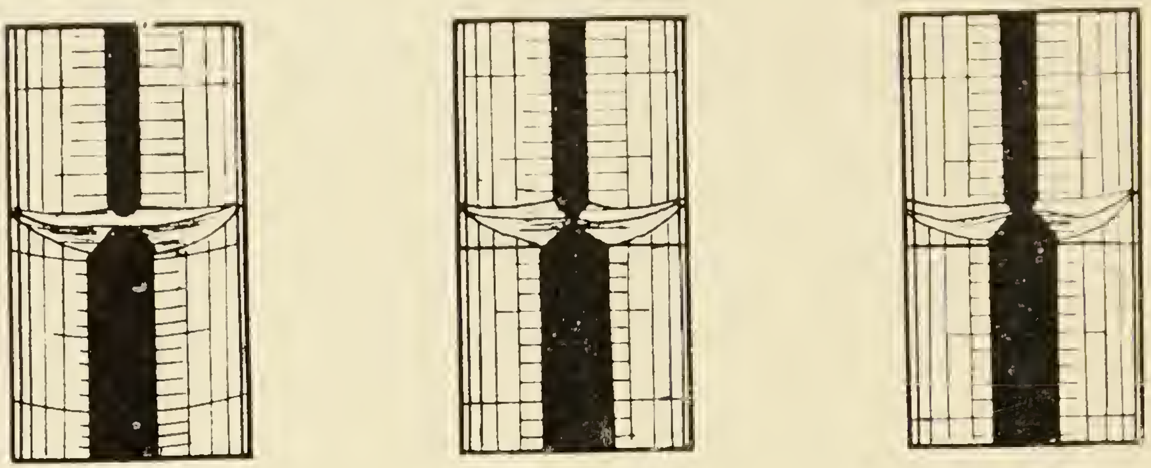
[1] B. Reinitzer, *Zeit. angew. Chem.*, 7. 547, 573, 643, 1894.

[2] J. H. M'Mahon (*Chem. News*, 45. 109, 1882; F. A. Gooch, *Amer. J. Science* (3), 44. 239, 1892; P. Kusnetzoff, *Zeit. anal. Chem.*, 46. 515, 1907; A. Prinzl, *Deut. Amer. apoth. Ztg.*, 4. 637, 1885; F. Köhler, *Brit. Pat. No.* 10936, 1903) recommends a small mirror on the surface of which are pasted two parallel strips of black paper each, say, 2 in. long and ½ in. wide, with a space about ½ in. wide between them. When reading, place the mirror behind and in contact with the burette, in such a position that the reflection of the eye can be seen in the space between the strips of paper. This ensures the eye being at right angles to the burette; J. F. Sacher, *Chem. Ztg.*, 35. 622, 1911.



Eye too low. Eye correct. Eye too high.

Fig. 13.—Meniscus errors

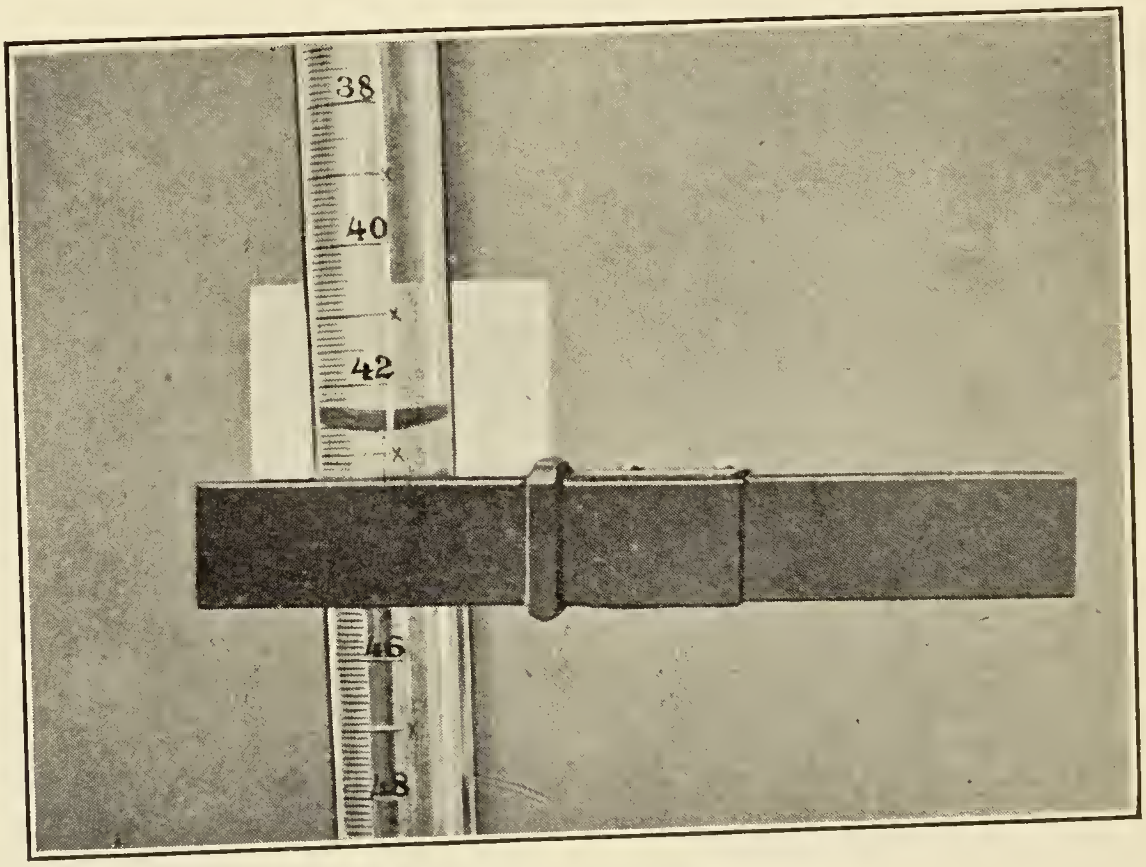


Fig. 14.—Göckel's burette screen.

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[1] P. Schellbach, *Chem. Ztg.*, **8.** 1515, 1885 ; J. Milbauer, *ib.*, **35.** 419, 1911 ; J. F. Sacher, *ib.*, **35.** 622, 1911 ; Goetze, *Zeit. anal. Chem.*, **50.** 373, 1911. It will be noticed that Schellbach's burette does not read the lowest level of the meniscus.

[2] Vernier burettes—C. Meinecke, *Chem. Ztg.*, **16.** 792, 1892 ; A. F. Reid, *Chem. News*, **65.** 125, 1892.

[3] Some testing stations refuse their imprimatur on these burettes.

Göckel's screens[1] (fig. 14) are quite satisfactory for reading the level of opaque liquids, and for avoiding the parallax errors in other solutions. The Göckel screen is a blackened clamp which grips the burette two or three millimetres below the level of the meniscus. The blackened part cuts off extraneous light from below, and leaves a sharp boundary-line at the meniscus. A sheet of white paper held behind the burette or fixed on to Göckel's screens as shown in the diagram still further emphasises the meniscus. A reading is made with the eye placed so that the front and back edge of the screen coincide. The Göckel's screen is also useful for avoiding parallax errors with opaque liquids where the meniscus is not visible.

Burette Floats.—Cylindrical floats arranged to swim on the surface of the liquid in the burette are marked so that the juxtaposition of the mark on the float with the graduations of the burette gives the required reading. The floats are supposed to eliminate dangers from parallax errors, and troubles with the meniscus. The ordinary Erdmann's float[2] is a plain cylinder. It has a tendency to stick to the inner walls of the burette, and is also inclined to assume an oblique position in the burette if it is not perfectly weighted. The simple float has therefore been condemned. Volhard placed a number of glass spines over the outer wall of Erdmann's float, with the idea of preventing the float sticking to the inner walls of the burette. Beutell's spherical floats[3] furnish good results provided they are properly weighted so as to swim vertically in the liquid. It is possible to read to 0·01 c.c. in a good burette with a good Beutell's float—provided the bore of the tube is not too wide, and the burette is suitably graduated. This float sticks to the side of the burette when the burette is emptied, and therefore, when the burette is to be refilled, the float must be taken out, carefully cleaned, and returned to the liquid. Diethelm[4] added an extra bulb to Beutell's float with the idea of making it unnecessary to remove the float every time the burette is refilled. In Rey's float, a small second bulb projects above the surface of the liquid and carries a mark. Hence, this float can be used for opaque liquids and dark-coloured solutions. The mark on the bulb above the surface of the liquid is used for reading differences of level of the liquid in the burette. The principal objection to floats is the difficulty in getting them properly weighted. A float which works satisfactorily with one liquid may be quite unsuited for another. There is an element of chance in purchasing a good float.

§ 16. The Calibration of Standard Flasks.

Just as in gravimetric work the accuracy of the weights is not to be taken on trust, so must the exactness of the measuring apparatus in volumetric analysis be established by trial. It is not at all uncommon to find that the weights in a laboratory have been the subject of wise scepticism, while the volumetric instruments have been accepted with blind faith, and conversely.

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[1] H. Göckel, *Chem. Ztg.*, **27**. 1036, 1903; J. Bergmann, *ib.*, **11**. 853, 1898; G. Lunge, *Zeit. angew. Chem.*, **17**. 198, 1904; G. Kottmayer, *Zeit. anal. Chem.*, **30**. 327, 1891.

[2] O. L. Erdmann, *Journ. prakt. Chem.* (1), **71**. 193, 1857; J. Volhard, *Liebig's Ann.*, **176**. 240, 1875; A. Schulze, *Zeit. anal. Chem.*, **21**. 167, 1882; **26**. 626, 1887; A. Gawalovski, *ib.*, **38**. 237, 1899; **22**. 240, 1883; R. Benedikt, *Chem. Ztg.*, **16**. 217, 1892; N. Wolff, *ib.*, **13**. 389, 1889; F. Musset, *Pharm. Centr.* (3), **16**. 459, 1885. C. Meissner (*Chem. Centr.* (3), **18**. 135, 1887) has a float fitted with a thermometer.

[3] A. Beutell, *Zeit. angew. Chem.*, **2**. 8, 1889.

[4] B. Diethelm, *Chem. Ztg.*, **26**. 607, 1902; H. Rey, *Ber.*, **24**. 2098, 1891; L. W. Andrews, *Zeit. anorg. Chem.*, **26**. 179, 1901; J. Wagner, *Zeit. phys. Chem.*, **28**. 193, 1899; P. Kreitling, *Zeit. angew. Chem.*, **13**. 829, 990, 1900; **15**. 4, 1902; W. Schlösser, *ib.*, **16**. 953, 962, 977, 1004, 1903; G. Lunge, *ib.*, **13**. 936, 1900; H. Thiele, *Zeit. öffent. Chem.*, **6**. 172, 1902.

It matters little what litre be adopted as a standard, but *it is of the greatest importance to have the pipettes, burettes, and measuring flasks rigorously consistent with one another.* The litre flask, for example, must hold 10 times as much as the 100-c.c. flask; 20 times as much as the 50-c.c. pipette; 200 times as much as the 5-c.c. pipette; etc.

Quite satisfactory calibrations are made by the National Physical Laboratory and other recognised testing stations, although some chemists prefer to test or calibrate their own apparatus. True, this may not be done with the precision exercised by officials accustomed to the work with every facility close at hand; but pipettes and burettes may be quite satisfactorily calibrated with the regular laboratory outfit.[1] The calibration of litre flasks requires a balance large enough to weigh a kilogram of water, and sensitive enough to indicate 0·02 grm. An ordinary analytical balance will suffice for small flasks.[2]

A litre flask with a long cylindrical neck, between 14 and 20 mm. in diameter, is thoroughly cleaned[3] and dried. The empty dry flask is balanced by a suitable tare. Fill the flask with distilled water until the lowest point of the meniscus is in the same horizontal plane as the mark on the neck. Let the flask stand in the balance case until the temperatures of the air and water are within 1°. Adjust the level of the water in the flask. Remove any excess of water by a piece of capillary tube. Do not allow drops of water to adhere to the interior neck of the flask; if any should be present, they may be removed by means of a piece of filter paper tied round the end of a glass rod. Weigh the flask and contents. Take the temperature of the water with a thermometer reading to 0·1°. The mean of three weighings may be taken as the correct value.

Suppose the mean of three weighings to be 998·95 grms. (brass weights in air); temperature of the water 15°; barometer, 760 mm. Since a litre of air at 15° and 760 mm. weighs 1·13 grms., the flask—by formula (2), page 32—will weigh $998·95 + 1·13 = 1000·08$ grms. The brass weights have probably been adjusted for weighing in air. In that case, we neglect the air displaced by the weights. If the weights have been reduced to weight *in vacuo*, we must make an allowance as indicated page 23.[4] It is not necessary to have the temperature of the water just 15°. When we know the weight of a given volume of water under any conditions of temperature, it is easy to calculate the corresponding amount of water for any standard temperature from Table VII., page 29.

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[1] As a rule, the analytical chemist cannot spare much time for calibrating his apparatus, and the cost in time will be greater than the charge made by the National Physical Laboratory, which has every facility for doing the work quickly.

[2] H. N. Morse and T. L. Blalock, *Amer. Chem. Journ.*, **16.** 479, 1894; A. Gawalovski, *Chem. Centr.* (3), **10.** 236, 1879; A. Démichel, *Rev. Anal. Chim.*, **5.** 1897; A. Mulder, *Chem. Weekblad*, **5.** 830, 1908.

[3] CLEANING VOLUMETRIC APPARATUS.—Grease is the great foe of accuracy in volumetric work. Thorough freedom from grease is very important. The smallest trace of grease may distort the meniscus and alter the amount of water retained as a film on the glass. The error so introduced may amount to 0·01 to 0·04 per cent., according to the method used in cleaning the vessel. To clean flasks, pipettes, or burettes, wash the vessel thoroughly with a concentrated aqueous solution of caustic soda; rinse with water; wash with a solution of chromic acid or potassium bichromate in sulphuric acid; and thoroughly rinse with distilled water. Flasks, etc., seem to gradually acquire a greasy film on their inner surface while in use. In some cases, the grease can be traced to the contamination of the distilled water by the oily packing between the "worm" and "still-head" of the still. If grease be absent, the surface of the glass will remain covered with a continuous film of water until all is removed by evaporation. If the water collects in drops instead of adhering as a continuous film, the vessels are greasy and want cleaning. W. O. Atwater and C. D. Woods, *Journ. Anal. App. Chem.*, **I.** 373, 1887; C. Mohr, *Chem. Ztg*, **II.** 561, 1887; W. Glenn, *Journ. Amer. Chem. Soc.*, **22.** 302, 1900; J. Walz, *Dingler's Journ.*, **207.** 427, 1873. M. Vandevyver (*Rev. Anal. Chim.*, **5.** 1897) shows that the errors due to variations in surface tension are reduced to a minimum if perfectly clean vessels are used.

[4] An error of 0·1 in the density of the brass weights (8·4) will produce an error of about 0·0017 grm., that is, 0·00017 per cent.

The above procedure can be followed for graduating a flask to contain ("Einguss") a specified volume. A narrow strip of paper is gummed longitudinally on the neck, the flask is weighed empty, and then filled part way up the neck with water, weighed, and a light mark made with a lead pencil on the strip of paper corresponding with the horizontal plane at the lowest point of the meniscus. If the first trial be not correct, add more or less water and make another mark; if this be inaccurate, make another trial, and repeat, if necessary, until it is correct. In this way the right volume can soon be obtained. A distinct line is then made on the strip of paper. The flask is then emptied. The paper above the last mark is cut away, and the neck of the flask, where the mark is to be etched, is warmed, and coated with a uniform layer of wax.[1] Starting from the top of the paper, a mark is carried uniformly round the neck of the flask with the blade of a pocket-knife, so as to expose a line of glass not protected by the wax.

The "ringing" of the neck is best performed by placing the mouth of the flask on a conical plug so placed that the left hand can rotate the flask while the right hand is used for cutting the ring (fig. 15). The hand with the knife[2] is supported and guided by blocks of wood at a suitable height. The operation is shown by photograph, fig. 15.

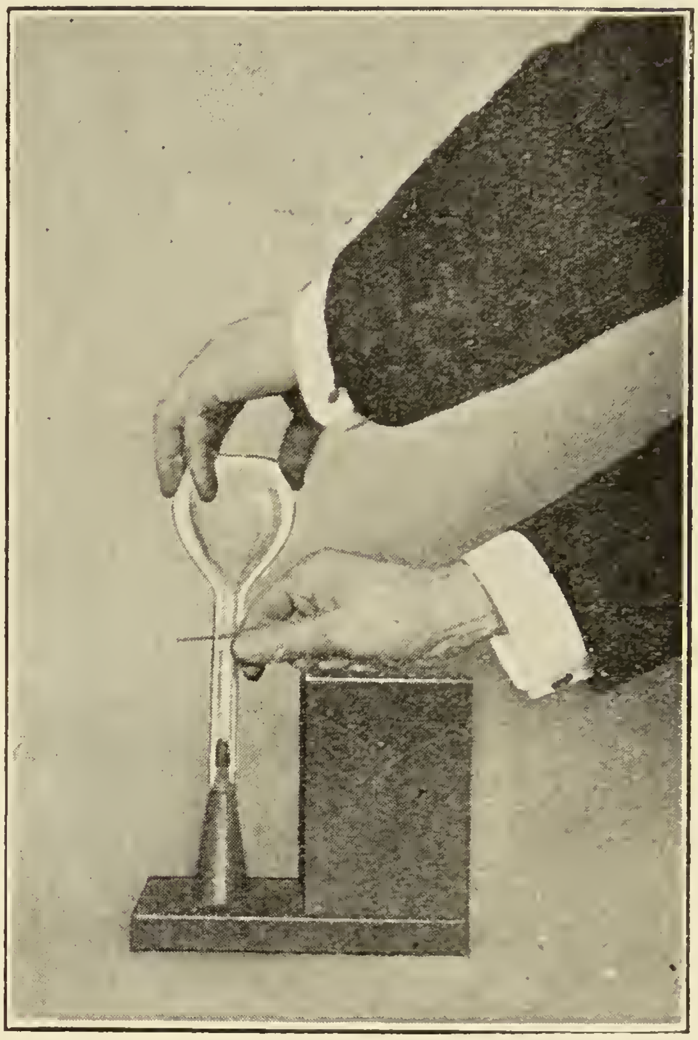

Fig. 15.—"Ringing" flasks.

A drop of hydrofluoric acid is then placed on the line while the neck of the flask is held horizontally. The drop is allowed to flow all round the neck on the exposed line by rotating the flask. In two or three minutes, the acid is washed off, the wax removed by wiping the hot wax with a cloth, and cleaning off the last traces of wax by means of methylated spirit.

When the flask is to be graduated "to deliver" ("Ausguss"), the contents are poured into a vessel of known weight and weighed. The temperature is taken just after the weighing. The entire neck should be wetted and drained into a flask at least one minute before pouring. With flasks marked "Contain," the neck should be dry above the meniscus, except for the wetting necessary to secure a constant meniscus of normal shape. The flask is held in an inclined position, so that the bottom and the parts near the neck may drain. At the end of a minute, the suspended drop is removed with a glass rod and included in the amount delivered.

The "error" allowed by most of the testing stations for measuring flasks is as follows:—

Capacity	50	100–250	300–500	500–1000	2000	c.c.
Permitted error (Contain) .	0·05	0·1	0·15	0·3	0·5	c.c.
Permitted error (Deliver) . .	0·1	0·2	0·3	0·6	1·0	c.c.

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[1] A mixture of equal parts of paraffin wax and carnauba wax, or beeswax alone—page 634.

[2] Or engraving tool. For a more elaborate apparatus, see C. B. Williams, *Journ. Amer. Chem. Soc.*, 24. 246, 1902.

§ 17. The Drainage or Afterflow from Measuring Vessels.

The drainage of measuring apparatus is of great importance. Schlösser[1] has established a relation between the time the discharge is stopped and the amount—afterflow—subsequently drained from the sides. The drainage is greater the more rapid the discharge of the liquid. When the discharge from a burette is 0·7 cm. per second, the afterflow during the first two minutes after stopping the outflow was found to be about 0·05 c.c. When the time of the discharge from the burette was changed from 65 to 125 seconds, an increase of 0·05 c.c. in the volume of the afterflow was obtained. Hence, if 0·05 c.c. of the standard solution will appreciably affect the result, it is necessary to work under standard conditions, and pay attention to the time of outflow of all apparatus marked "Deliver" ("Ausguss")—burettes, pipettes, flasks, etc.

The rate of outflow for burettes and measuring pipettes is limited by the size of the tip, and it is usual to make the tip so that the time of outflow is not greater than three minutes, nor less than the numbers indicated in the following table:—

Length graduated . .	65	60	55	50	45	40	35	30	25	20	15	c.c.
Time of outflow . .	140	120	105	90	80	70	60	50	40	35	30	secs.

When titrating and standardising burettes, it is well to wait a couple of minutes[2] before every reading in order to give the sides time to drain.

The amount of liquid which adheres to the walls of a burette, etc., is dependent upon (1) the viscosity of the fluid; (2) the adhesion of the liquid to the walls of the vessel; which in turn depends partly upon (3) the cleanliness of the walls; (4) on the surface exposed to the liquid; (5) on the rate of outflow from the jet of the burette,[3] etc.

In illustration, contrast alcohol with concentrated sulphuric acid. Again, a pipette which delivered 100 c.c. of water at 15·5°, with a drainage of 10 seconds, and then touching the delivered liquid with the point of the pipette,[4] delivered the volumes indicated in the accompanying Table IX. when the solutions indicated were employed in place of water:—

Table IX.—Effect of the Nature of the Liquid on the Volume delivered by a Pipette.

Solution.	Specific gravity.	Volume delivered.
Zinc sulphate	1·4246	99·52
Sodium chloride	1·2072	99·73
Ammonium sulphate	1·2500	99·75
Potassium chloride	1·1812	99·82
Ammonium chloride	1·0724	99·95
Water	1·0000	100·00

Hence it is obvious that a pipette graduated for water delivers a sensibly different volume when applied to other liquids. Pipettes may be used interchangeably for solutions not exceeding normal concentration provided the time of outflow be the same as that allowed for pure water. But a pipette or burette which delivers a volume of liquid which differs appreciably from water, requires a special calibration with that particular liquid in place of water.

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[1] W. Schlösser, *Zeit. angew. Chem.*, **16**. 953, 977, 1904, 1903; N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, **4**. 553, 1908; T. Milobendzki, *Zeit. anal. Chem.*, **46**. 20, 1907.

[2] H. von Jüptner (*Chem. Ztg.*, **8**. 1766, 1885) recommends three minutes' drainage for alcohol and water. See also T. Milobendzki, *Zeit. anal. Chem.*, **46**. 20, 1907.

[3] J. Mulder, *Die Silberprobirmethode*, Leipzig, 1859.

[4] R. R. Tatlock, *Chem. News*, **23**. 14, 1871; A. Schulze, *Zeit. anal. Chem.*, **21**. 167, 1882.

According to Schlösser,[1] the effect of temperature on the drainage is negligibly small between 15° and 30°.

§ 18. The Calibration of Pipettes.

It is generally cheaper to purchase ungraduated pipettes and mark them according to the following scheme.[2] First thoroughly clean the pipette by sucking caustic soda into it by means of a rubber tube and pinchcock. Follow by rinsing with water, etc., as indicated page 36. Fasten a narrow strip of paper longitudinally to the upper part of the tube. Tare a small beaker of water on the balance and suck water from the beaker into the pipette until the beaker has lost the necessary amount of water for the capacity of the pipette. Mark the position of the lower level of the meniscus with a lead pencil on the paper strip. Run the liquid into a weighed stoppered flask. Hold the pipette vertically during the outflow and let it drain 15 seconds. Remove the suspended drop by contact with a wet surface (side of flask) and include it with the delivered amount.[3] Weigh the flask and its contents. If the amount of liquid delivered from the pipette be too large or too small, mark the paper below or above the first mark, and repeat the filling and weighing until finally the weight of liquid discharged from the pipette is exactly the amount desired at the stated temperature. The pipette may be marked with a writing diamond, the paper removed and the pipette marked all round with the diamond, or the mark may be etched with hydrofluoric acid as indicated for "ringing" flasks.[4] Now verify the accuracy of the graduation by filling the pipette as before.[5]

The "error" in pipettes allowed by testing stations is usually as follows:—

Capacity	1 to 2	10	25	50	100–200	c.c.
Permitted error	0·01	0·02	0·03	0·05	0·1	c.c.

It is easy to buy pipettes far more accurate than this.

§ 19. The Calibration of Burettes.

The burette is a most important instrument used in volumetric analysis. Burettes can be purchased accurate to 0·02 c.c. A bad burette is a nuisance, and is best discarded. To calibrate a burette, fill the burette with distilled water at the normal temperature, and withdraw successive portions ranging from 2 to 5 c.c. into a tared flask. By weighing these quantities—accurate to a milligram—the volume delivered by the burette between any two divisions can be readily determined. If a number of burettes have to be calibrated, the following procedure, based upon Scheibler's and Ostwald's methods,[1] is sufficiently exact, and it will save time.

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[1] W. Schlösser, *Zeit. anal. Chem.*, **46**. 392, 1907; W. Schlösser and C. Grimm, *Chem. Ztg.*, **30**. 1071, 1906.

[2] F. Clowes, *Journ. Soc. Chem. Ind.*, **11**. 327, 1892. For the graduation of glass vessels, C. Foord, *Chem. News*, **30**. 191, 1874; M. C. Lea, *Amer. J. Science* (2), **42**. 373, 1866; R. Bunsen, *Gasometrische Methoden*, Braunschweig, 28, 1877.

[3] Emptying Pipettes.—Pipettes may be emptied in at least four ways: (1) the liquid is allowed to run from the pipette without touching the pipette against the sides of the vessel: (2) by blowing out the last drop (Ostwald). This method is useful in dealing with capillary pipettes; (3) by touching the point of the pipette against the surface of the solution; and (4) by touching the point of the pipette against the side of the vessel (*a*) all the time the pipette is emptying, (*b*) at the end of the discharge (Fresenius; Treadwell). The same method of work must be employed when the pipette is in use as is employed during standardisation. H. Göckel, *Chem. Ztg.*, **25**. 1084, 1901; **26**. 159, 1902; *Zeit. angew. Chem.*, **15**. 707, 1902; **16**. 49, 562, 1903; W. Schlösser, *ib.*, **16**. 977, 1903; L. A. Fischer, *Journ. Amer. Chem. Soc.*, **20**. 912, 1898; N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, **4**. 553, 1908.

[4] A simple modification of the apparatus, fig. 15, enables this to be done neatly and quickly.

[5] C. B. Williams, *Journ. Amer. Chem. Soc.*, **24**. 246, 1902.

A glass pipette is cut from an old pipette (about 2 c.c.), as shown, and mounted with the burette to be tested by means of pressure tubing and stopcocks (or pinchcocks), as shown in the diagram, fig. 16. Two marks, *a* and *b*, respectively below and above the bulb, are cut or etched on the stem of the pipette. The pipette and the burette are thoroughly cleaned. The whole is mounted as

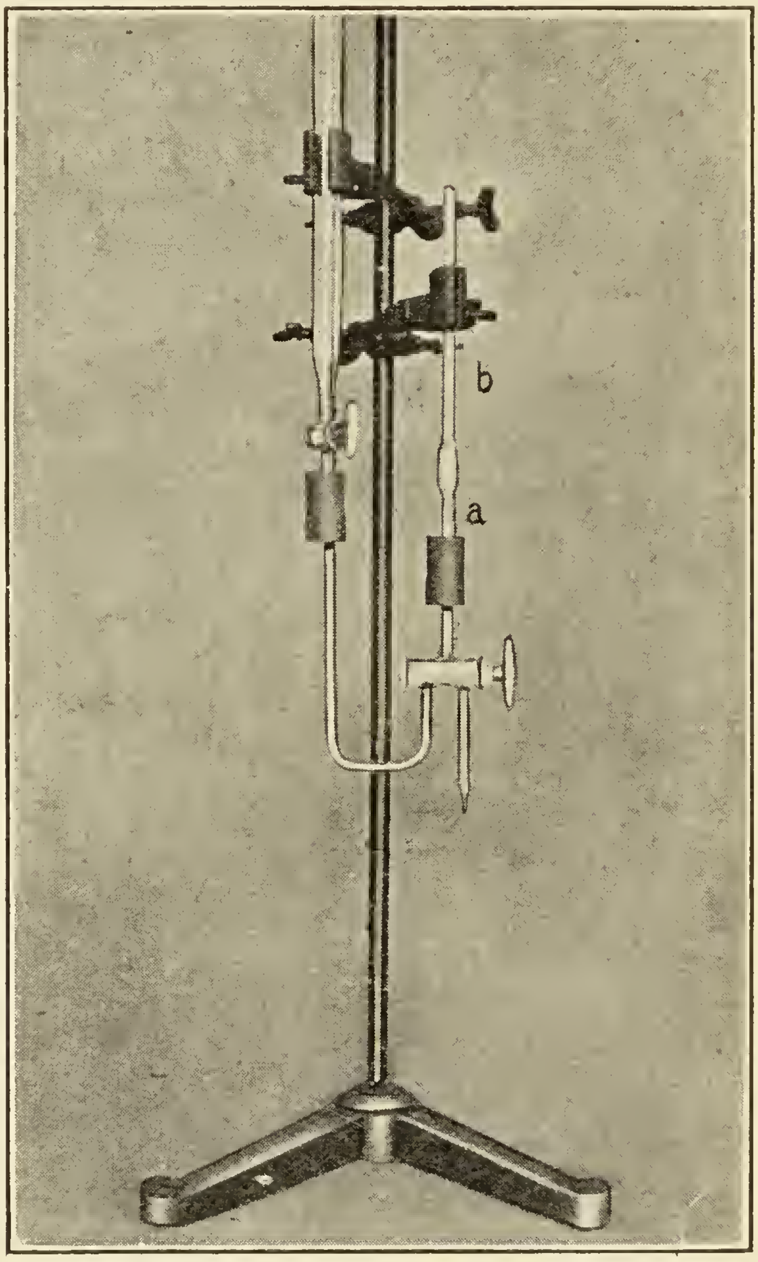

Fig. 16.—Calibration of a burette.

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[1] C. Scheibler, *Journ. prakt. Chem.* (1), **76**. 177, 1859 ; W. Ostwald, *ib.* (2), **25**. 453, 1882 ; W. Ostwald and R. Luther, *Ausführung physiko-chemischer Messungen*, Leipzig, 87, 1894 ; T. W. Richards, *Journ. Amer. Chem. Soc.*, **22**. 144, 1900 ; H. N. Morse and T. L. Blalock, *Amer. Chem. Journ.*, **16**. 479, 1894 ; D. W. Horn and E. M. van Wagener, *ib.*, **30**. 196, 1903 ; O. von Spindler, *Schweiz. Woch. Chem. Pharm.*, **46**. 145, 1908 ; L. W. Andrews, *ib.*, **28**. 491, 1902 ; D. W. Horn and E. M. van Wagener, *ib.*, **30**. 96, 1903 ; H. L. Payne, *Journ. Anal. App. Chem.*, **6**. 326, 1892 ; M. J. C. Boot, *Rec. Trav. Pays Bas*, **13**. 417, 1894 ; D. Carnegie, *Chem. News*, **64**. 42, 1891. W. Ostwald (*l.c.*) ; and A. S. Cushman (*Journ. Amer. Chem. Soc.*, **23**. 482, 1901) use a pipette with the upper stem graduated. The error is read directly on the graduated stem of the pipette every time the pipette is filled with, say, 2 c.c. of liquid from the burette. This pipette is easily obtained by using one of Cobbett's pipettes instead of that indicated in the text. For calibrations with mercury, C. A. Bell, *Proc. Chem. Soc.*, **17**. 179, 1901 ; *Chem. News*, **83**. 21, 1901.

shown in the diagram. Take care that the tubes are quite vertical. The burette, the tubes between the burette and the pipette, and the jet of the pipette are filled with pure water. Water is run into the pipette from the burette until the lower level of the meniscus is in the same horizontal plane as the lower mark of the pipette. The burette is filled to zero. Water is run from the burette until the pipette is filled to the mark *b*. Read the burette. This water is then discharged from the pipette. The filling and emptying of the pipette is continued until insufficient water remains in the graduated portion of the burette to fill the pipette. The burette is read each time the pipette is filled. Two minutes are, of course, allowed for drainage, as indicated above.

Suppose that the 50-c.c. burette has filled the pipette 16 times, and, as a mean of three comparisons, the burette reads 49·64 c.c. The burette is then refilled, and exactly the same amount of water is run from the burette into a weighed flask. The weight of water gives the necessary data for calculating the volume of the pipette. Suppose we get a weight of 49·64 grms. at 18·5°. From the table, page 29, we see that the density of water at this temperature is 0·9985, and its volume is therefore 49·64 ÷ 0·9985 = 49·71 c.c. Hence,

$$\text{Volume of water in pipette } (18\cdot5^\circ) = \frac{49\cdot71}{16} = 3\cdot107 \text{ c.c.}$$

Suppose that the numbers in the second column of Table X. represent the successive readings of the burette under the conditions just indicated. The numbers in the third column of Table X. will represent the corresponding volumes, that is, the product of 3·107 with the corresponding number in the first column. The fourth column gives the error of the readings indicated in the second column.

Table X.—Burette Corrections—Burette No. 5.

Number of reading.	Burette reading.	Corrected burette reading.	Corrections.
	c.c.	c.c.	c.c.
1	3·11	3·11	0·00
2	6·20	6·21	+0·01
3	9·28	9·32	+0·04
4	12·39	12·43	+0·04
5	15·51	15·53	+0·02
6	18·61	18·64	+0·03
7	21·72	21·75	+0·03
8	24·53	24·57	+0·04
9	27·92	27·96	+0·04
10	31·02	31·07	+0·05
11	34·13	34·18	+0·05
12	37·24	37·28	+0·04
13	40·34	40·39	+0·05
14	43·44	43·50	+0·06
15	46·63	46·69	+0·06
16	49·64	49·71	+0·07

These numbers can be plotted on squared paper (fig. 17): ordinates, corrections (column 4); abscissæ, volumes (column 2). Hence the correction for any reading of the burette can be seen at a glance. In the present example, the burette reads 49·64 when the corresponding volume is 49·71 c.c. Hence that burette reading is to be corrected by + 0·07 c.c. Had the corrected reading for another burette been 49·59 c.c., the actual burette reading 49·64 c.c. would have been corrected by – 0·05 c.c. The sign of the correction wants thinking over. This burette is unsatisfactory—probably the bore of the tube is not uniform.

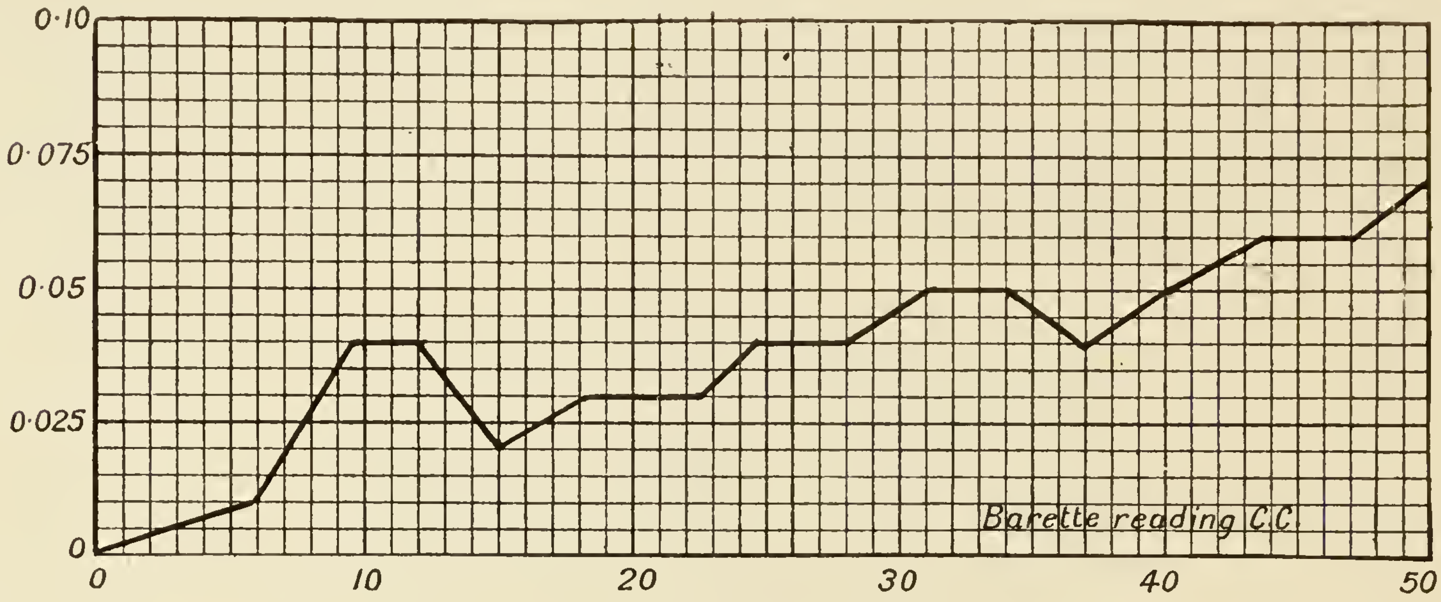

Fig. 17.—Corrections for burette No. 5.

Example.—At the beginning of a titration, the burette read 3·69 c.c. ; at the end, 20·06 c.c. From the graph (fig. 17) of the above table, 3·69 c.c. represents 3·70 c.c. and 20·06 represents 20·09 c.c. The difference 20·09 – 3·70 = 16·39 c.c. represents the number of cubic centimetres of fluid run from the burette at 18·5°. If the solution be standardised at 15°, another correction must be made (page 29).

The following "errors" are usually "permitted" at a standard testing station :—

Capacity . . .	1 to 2	2 to 10	10 to 30	30 to 50	50 to 100 c.c.
Permitted error . .	0·01	0·02	0·03	0·05	0·10 c.c.

For parts of the volume less than half the total content, the limits of error are one-half the above. Burettes are usually tested at five points at the National Physical Laboratory. Charge : 2s. to 2s. 6d., and 6d. for each additional point.

The burette nozzle should be such that the time of delivery of the burette does not exceed 10 seconds. Wagner (*l.c.*) thinks that 70 seconds is sufficient for the time of outflow. It might also be added that Förster[1] noticed that burettes which have been used with alkaline solutions increase perceptibly in volume. Thus, one is mentioned which changed from 50 c.c. to 51 c.c. after being in use for a year. Such burettes must be frequently calibrated.[2]

§ 20. Burette Stands, and Burette Cocks.

The burette, when in use, should be clamped vertically to a firm stand. The simpler types of stand are usually the best. It is, however, important to select those clamps which hide as little of the scale as possible. Kaehler's[3] clamp, shown in fig. 9, is excellent. Vosâtka's stands (fig. 18) hide none of the scale. Other clamps are shown in different parts of this work. The points to be kept in view when selecting a burette stand are: (1) rigidity; (2) clear scale; (3) simple mechanism; and (4) vertical adjustment.

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[1] O. Förster, *Chem. Ztg.*, **28.** 147, 1904.

[2] For general reports on volumetric apparatus, see *Mitt. der K.N.E.K.*, **3.** 5, 1908 ; *Internat. Kong. angew. Chem.*, **7.** 41, 1909.

[3] M. Kaehler, *Zeit. anal. Chem.*, **11.** 190, 1872 ; J. Dietl, *ib.*, **15.** 186, 1876 ; C. Kippenberger, *ib.*, **43.** 233, 1904 ; A. Eiloart, *ib.*, **33.** 205, 1894 ; A. Gawalovski, *ib.*, **38.** 237, 1899 ; R. Pribram, *ib.*, **12.** 299, 1873 ; F. Allihn, *Chem. Ztg.*, **10.** 647, 1886 ; J. Vosâtka, *ib.*, **28.** 795, 1904 ; F. Oettel, *ib.*, **19.** 1384, 1895 ; L. Weinstein, *ib.*, **8.** 1870, 1885 ; A. T. Lincoln, *Journ. Amer. Chem. Soc.*, **27.** 1442, 1905 ; F. J. P. van Calker, *Dingler's Journ.*, **225.** 84, 1878 ; R. Muencke, *ib.*, **229.** 336, 1879 ; G. Müller, *Zeit. angew. Chem.*, **21.** 2318, 1908.

Burettes are supplied with funnel-like tops[1] (fig. 18) for a few pence extra. This enlargement of the tube is convenient for filling. The contents of the burette must be protected from dust. Loose glass caps like inverted test-tubes, or glass spheres, are convenient for keeping out dust, etc., when the burette is in use.

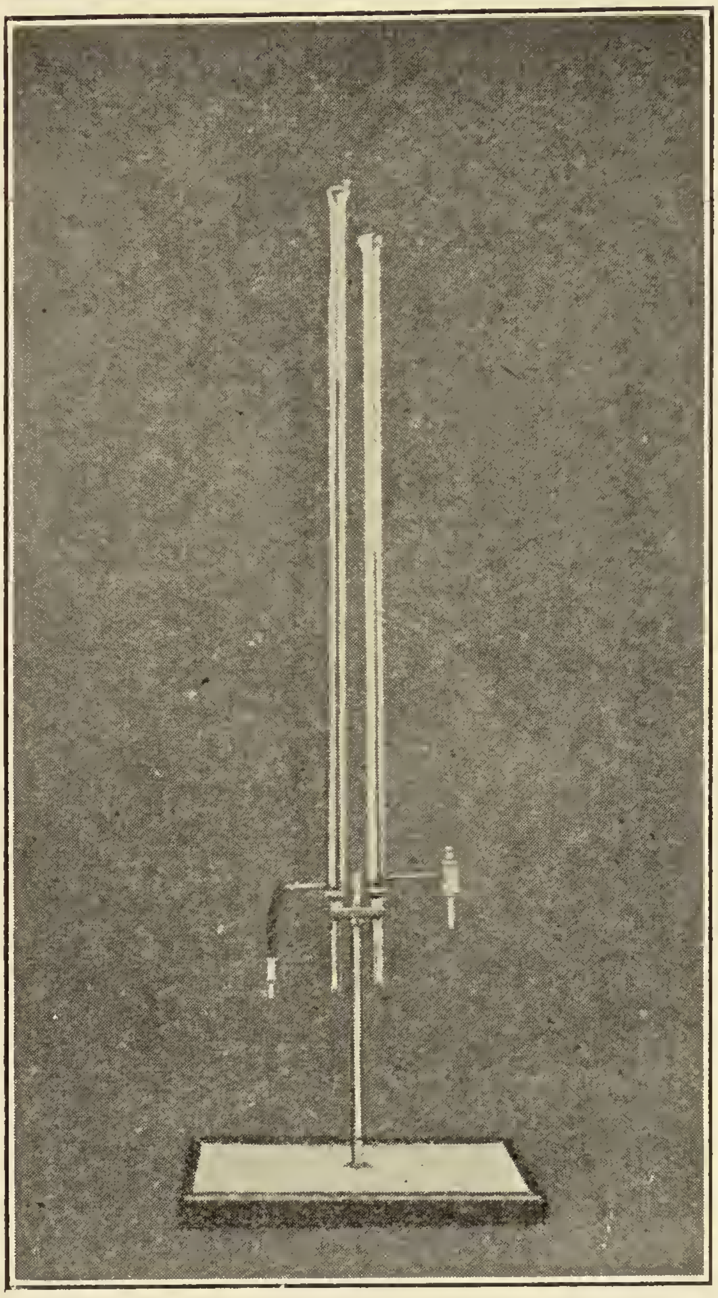

Fig. 18.—Vosâtka's burette stand.

Burettes are now usually fitted with glass stopcocks—the plain straight cock, fig. 16, left; Geissler's cock, fig. 18, right; Meissner's cock[2]; or Greiner and Friedrichs' cock, fig. 24. The latter are also arranged with three ways to connect the burette either with the outflow jet or with the stock of standard solution. Glass cocks are a nuisance when they begin to leak, as they often do, after they have been in use some time.[3] The glass between the two openings of the bored plug gets worn. Hugershoff's cocks[1] (fig. 19) overcome this difficulty. Burettes with glass cocks are nearly always used for permanganate solutions (see also page 197). Permanganate solutions are not used with rubber tube and pinchcock (fig. 18, left). Glass stopcocks are not used for caustic alkali solutions on account of the tendency of the stopcock to stick, but they are used for iodine, and permanganate solutions.[2] The rapid wear of glass cocks with caustic alkaline solutions also causes the cock to leak very soon.[3] Rubber tube and glass jet with (old-fashioned) metal pinchcock may be used for caustic alkali solutions and solutions which do not attack rubber.[4] The plug cocks are better than the metal pinchcocks.[5] Plug cocks are made by plugging a piece of rubber tube with a glass bead, or bit of glass rod (fig. 18, left, and fig. 20) about 8 mm. long. By squeezing the tube around the plug, a channel is made for the passage of the liquid. Binder's nozzle, shown in fig. 21, is made from a piece of capillary tube by sealing up one end, and blowing a hole at the side. It too is opened by pinching or squeezing the rubber tube. Both these cocks are excellent.

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[1] A. C. D. Poole, *Brit. Pat. No.* 470129.

[2] C. Meissner, *Zeit. anal. Chem.*, **26**. 625, 1887; E. Greiner and Friedrichs, *ib.*, **26**. 49, 1887; **27**. 470, 1888.

[3] Lubricants for Glass Stopcocks.—F. C. Phillips, *Journ. Amer. Chem. Soc.*, **20**. 149, 1898; *Chem. News*, **78**. 311, 1898. According to L. L. de Koninck and M. Lejeune (*Bull. Soc. Chim. Belg.*, **23**. 79, 1909) stopcock burettes for iodine and permanganate solutions may be safely greased with vaseline.

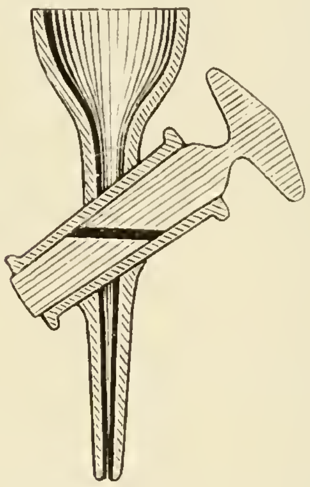

FIG. 19.—Hugershoff's glass cock.

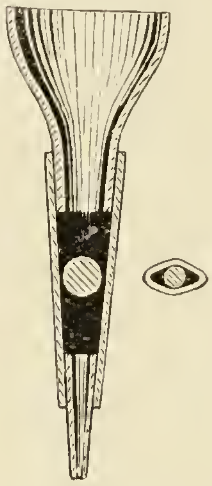

FIG. 20.—Plug cock.

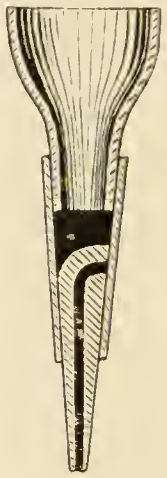

FIG. 21.—Binder's jet.

To avoid the inconvenience which arises when glass stopcocks fall out and break, C. E. Munroe[6] has designed a simple clip made of hard rubber sheet shaped so that it will encircle some part of the apparatus and grip a 2-pronged fork. The prongs grip the thinnest part of the stopper so as not to impede the motion of the stopper, and yet they hold it so securely as to prevent its falling out in whatever position the apparatus is held. Snelling recommends stoppers with a small groove cut in the extended portion. A rubber ring is fitted in the groove and affords complete security from the slipping of the cock from its place.

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[1] F. Hugershoff, *Chem. Centr.* (3), **18.** 135, 1887 ; C. Meissner, *Chem. Ztg. Rep.*, **12.** 65, 1888.

[2] L. L. de Koninck and M. Lejeune, *Bull. Soc. Chim. Belg.*, **23.** 79, 1909.

[3] P. Rudnick (*Journ. Amer. Chem. Soc.*, **32.** 971, 1910) proposes a silver stopcock for caustic solution. P. Fiebag (*Archiv Pharm.* (3), **22.** 544, 1885) used a tin stopcock.

[4] H. F. von Jüptner, *Oester. Zeit. Berg. Hutt.*, **28.** 33, 1880.

[5] F. Mylius, *Archiv Pharm.* (3), **3.** 151, 1874 ; F. Mohr, *Lehrbuch der Titriermethode*, Braunschweig, 1874 ; A. Lebrasseur, *Analyst*, **10.** 194, 1885 ; F. Sutton, *ib.*, **10.** 214, 1885 ; E. Thiele, *Zeit. anal. Chem.*, **40.** 405, 1901 ; J. Wallensteiner, *ib.*, **25.** 547, 1886 ; A. Gawalovski, *ib.*, **38.** 237, 1899 ; W. Leybold, *ib.*, **26.** 230, 1887 ; O. Binder, *ib.*, **27.** 178, 1888 ; C. Kippenberger, *Chem. Ztg.*, **27.** 1255, 1903.

[6] W. O. Snelling, *Journ. Ind. Eng. Chem.*, **4.** 613, 1912.

CHAPTER III.

VOLUMETRIC ANALYSIS.

§ 21. Normal Solutions.

In volumetric analysis[1] a standard solution of known strength is gradually added to a solution of the substance under investigation until the reaction between the two is completed. The volume of the standard solution required for this purpose is proportional to the amount of the substance in the solution under investigation. The two solutions must be of such a kind that the reaction takes place quickly and quantitatively. It must also be possible to recognise the end of the reaction. This is frequently indicated by a change in colour which occurs in the presence of a third substance, the **indicator**, immediately a small excess of the standard solution has been added. The indicator is usually indifferent to the main reaction. Since a definite amount of the standard solution can react with a definite amount of the substance under investigation; given the volume of the standard solution, the amount of the substance under investigation can be calculated by simple rule-of-three.

The standard solutions may be any strength, but it is convenient to make them of such a strength that the weight of the dissolved substance, per litre, bears a simple numerical relation to the molecular weight of the compound. *A solution which contains the hydrogen equivalent weight in grams of an element or compound per litre is called a* **normal solution**, written N-solution; a semi-normal solution is one-half the strength of a normal solution—$\frac{1}{2}$N-solution; a deci-normal solution—$\frac{1}{10}$N-solution—is one-tenth the strength of a normal solution; and a centi-normal solution—$\frac{1}{100}$N-solution—is one-hundredth the strength of a normal solution.

The "equivalent weight" of a substance is the number of grams of the substance which brings into reaction—combination or replacement—the equivalent of 1·008 grms. of hydrogen; 8 grms. of oxygen, etc. To illustrate further, the molecular and equivalent weights of HCl, $NaOH$, $NaCl$, $AgNO_3$, NH_4CNS, and $Na_2S_2O_3, 5H_2O$ are identical; the equivalent weights of $H_2C_2O_4$, H_2SO_4, $Ba(OH)_2$, and $CaCO_3$ are half the molecular weights; the equivalent weight of As_2O_3 is one-fourth the molecular weight; the equivalent weight of $KMnO_4$ in acid solution is one-fifth the molecular weight; and the equivalent weights of KIO_3 and $K_2Cr_2O_7$ are one-sixth the molecular weights.

It is not always easy to see how the equivalent weight of some of these substances is determined, hence a few illustrations may be cited. In titrating iodine solutions with sodium thiosulphate, the reaction is represented by the symbols: $2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$. Here one molecule of sodium thiosulphate is equivalent to one atom of iodine, which, in turn, is equivalent to one atom of hydrogen. Hence the equivalent of $Na_2S_2O_3 . 5H_2O$ is numerically equal to the molecular weight.

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[1] Following up some early suggestions by E. A. H. Descroizilles (1802) and L. N. Vauquelin (1812), J. L. Gay Lussac demonstrated the applicability and utility of volumetric methods in analytical chemistry—for chlorimetry, 1824; for alkalimetry, 1828; silver, 1832. See L. L. de Koninck, *Bull. Assoc. Belg. Chim.*, **19**. 28, 73, 422, 1904; *Histoire de la Méthode Titrimétrique*, Brussels, 1901.

With potassium bichromate, in titrating ferrous salts, we have the reaction: $K_2Cr_2O_7 + 6FeSO_4 + 7H_2O \rightarrow$ etc. This reduces to $3O + 6FeO \rightarrow 3Fe_2O_3$. Hence the potassium bichromate furnishes three atoms of oxygen, which, in turn, correspond with six atoms of hydrogen. Hence the molecule of potassium bichromate is equivalent to six atoms of hydrogen, or the equivalent is one-sixth the molecular weight.

The case of potassium permanganate is a little curious. When ferrous sulphate is oxidised by potassium permanganate in acid solution, the equation

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

reduces to

$$5O + 10FeO \rightarrow 5Fe_2O_3.$$

Or, two molecules of potassium permanganate furnish five atoms of oxygen, which are equivalent to ten atoms of hydrogen. Hence the normal solution of $KMnO_4$ will contain one-fifth of the molecular weight, that is, $\frac{1}{10}$ of $2 \times 158 = 31{\cdot}6$ grms. per litre. In Volhard's process for manganese, the titration is made in neutral solution. The reaction is

$$2KMnO_4 + 3MnSO_4 + 2ZnO \rightarrow 5MnO_2 + K_2SO_4 + 2ZnSO_4,$$

which reduces to

$$Mn_2O_7 + 3MnO \rightarrow 5MnO_2.$$

Or, two molecules of potassium permanganate give three atoms of oxygen, so that the normal solution contains one-sixth of twice $158 = 52{\cdot}66$ grms. per litre, or the equivalent weight is one-third the molecular weight. Hence there are two different normal solutions, depending on the particular reaction under consideration. But potassium permanganate is generally employed in acid solution, and in consequence, unless otherwise expressed, a normal solution of $KMnO_4$ is understood to contain 31·63 grms. per litre.[1]

Again, in titrating stannous chloride with ferric chloride, two molecules of the latter give two molecules of chlorine to one molecule of stannous chloride:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4.$$

Hence one molecule of ferric chloride is equivalent to one atom of chlorine, which, in turn, is equivalent to one atom of hydrogen. The molecular and equivalent weights are identical. A normal solution of stannous chloride, on the other hand, will have half the molecular weight of $SnCl_2$ expressed in grams per litre, because one molecule of stannous chloride takes two atoms of chlorine from two molecules of ferric chloride.

The preceding definition of normal solutions is virtually that given by F. Mohr in 1859.[2] This definition has been adopted by the leading writers on volumetric analysis (Fresenius, F. Sutton, E. F. Fischer, A. Classen), and most analysts. Other definitions have been proposed, and a few writers (N. Menschutkin, M. M. P. Muir, C. Winkler, J. Muter) have defined a normal solution to be a "solution containing the molecular weight of the salt in grams per litre." This definition is advantageously used in physical chemistry, but not in analytical chemistry. It might be noted *en passant* that Gay-Lussac's "normal solution of sodium chloride" is "a solution of sodium chloride such that 100 c.c. will exactly precipitate 1 gram of silver." This special definition is used in many assaying laboratories for these particular solutions.

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[1] For "the available oxygen" standard, see R. Abegg, *Anleitung zur Berechnung volumetrischer Analysen*, Breslau, 1900.

[2] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethode*, Braunschweig, 1859; W. Fresenius, *Zeit. anal. Chem.*, **25**. 205, 1886; B. Tollens, *ib.*, **25**. 363, 1886; C. Marx, *ib.*, **26**. 217, 1887; L. L. de Koninck, *ib.*, **25**. 487, 1886; A. H. Allen, *Chem. News*, **40**. 239, 1887; C. Winkler, *Die Maassanalyse nach neuen titrimetrischen System*, Freiburg, 1883; *Ber.*, **18**. 2527, 1885; *Zeit. anal. Chem.* **25**. 484, 1886.

§ 22. Standard Solutions of Hydrochloric Acid.

Hydrochloric acid—HCl. Molecular weight : 36·468 ; equivalent weight : 36·468.

The most commonly employed solutions are :

	Grm. HCl per c.c.
N-Hydrochloric acid	0·036468
$\frac{1}{2}$N-Hydrochloric acid	0·018234
$\frac{1}{5}$N-Hydrochloric acid	0·007291
$\frac{1}{10}$N-Hydrochloric acid	0·003647

To prepare a semi-normal solution of hydrochloric acid, that is, a solution of hydrochloric acid containing half the equivalent weight (viz. 18·25 grms.) per litre, make a solution rather more concentrated than is finally needed; determine the exact strength by comparison with another solution of known titre, or by analysis; and then dilute to the required strength. Never start with a solution more dilute than that finally required, because of the difficulties involved in measuring accurately small quantities of material.

Suppose that the hydrometer shows that the stock of concentrated acid has a specific gravity 1·14. From Table LXXVI., an acid of this strength has 28 per cent. of HCl by weight. Hence, 77 c.c. of this acid will have between 20 and 27 grms. of HCl. Make 77 c.c. of this acid up to 1100 c.c. in a Giles' flask[1] (fig. 22*c*) with recently boiled distilled water. Let the solution stand a few hours so that it may attain the temperature of the room. If the temperature of the room be not that indicated on the flask, an allowance must be made as indicated, Table VII., XI., or XIII.

Compact fragments of Iceland spar[2]—calcium carbonate—weighing from 2 to 3 grms. each, are broken from a large crystal by pressing the edge of the blade of a knife against a large clear crystal and tapping the back of the blade sharply with a hammer. These fragments are rinsed with dilute hydrochloric acid or nitric acid to free them from adhering powder, and to round their edges and corners. They are then well washed with distilled water, and dried in an oven at 110°. The pieces are preserved in a stoppered bottle for use.

Two or three pieces of the Iceland spar are placed in a clean dry beaker or

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[1] W. B. Giles, *Chem. News*, **69**. 99, 1894—fig. 22*c*. ; W. Wislicenus, *Ber.*, **29**. 2442, 1896—fig. 22*b*. These flasks are convenient when standard solutions are to be made up from reagents which cannot be exactly weighed. Ordinary litre flasks—fig. 22*e*—may of course be used, but the subsequent dilution is not so easily done. In Biltz's or Pflüger's flask (E. Pflüger, *Zeit. anal. Chem.*, **25**. 91, 1886)—fig. 22*d*—there is a bulb above the mark on the neck to facilitate shaking. With the latter flasks, the amount of concentrated acid taken must be adjusted for 1000 c.c. In the present case, 70 c.c. would have been taken for 1000 c.c. in place of 77 c.c. for 1100 c.c. A. Goske (*Chem. Ztg.*, **28**. 795, 1904) and E. Hirschsohn (*Zeit. anal. Chem.*, **30**. 95, 1891) describe a flask with a wide neck graduated in cubic centimetres between 920 and 1000 c.c.—fig. 22*a*. The use of this flask will be obvious, and it would have been as convenient as Giles' flask for our purpose. The wide neck, however, makes the "error of experiment" somewhat greater.

[2] Selected crystals are remarkably pure—more pure indeed than the regular "sodium carbonate purissimus" usually employed for standardising hydrochloric acid. This excellent method of standardising hydrochloric acid was recommended by G. Duerr, *Chem. News*, **28**. 156, 1873 ; O. Masson, *ib.*, **81**. 73, 1900 ; W. H. Green, *ib.*, **87**. 5, 1903.

Erlenmeyer's flask. Weigh the beaker and contents, all dried at 110° and cooled in a desiccator. Cover the beaker with a watch-glass, and add 20 c c. of the hydrochloric acid from the flask[1] by means of a clean pipette in such a way that there is no loss by spurting. When the evolution of gas has almost ceased (3–4 hours) rinse the side of the beaker with distilled water. Restore the cover, and heat the solution to near the boiling point on an asbestos pad or quartz plate for about an hour. This is to ensure that the reaction between the acid and the spar is complete. Bumping must not be permitted, or minute fragments may be detached from the undissolved spar which would cause high results. Decant off the solution, wash the beaker and the contained spar thoroughly with distilled water, dry the beaker and contents at 110°, cool in a desiccator, and weigh. This furnishes the data necessary for calculating the strength of the acid. For example:

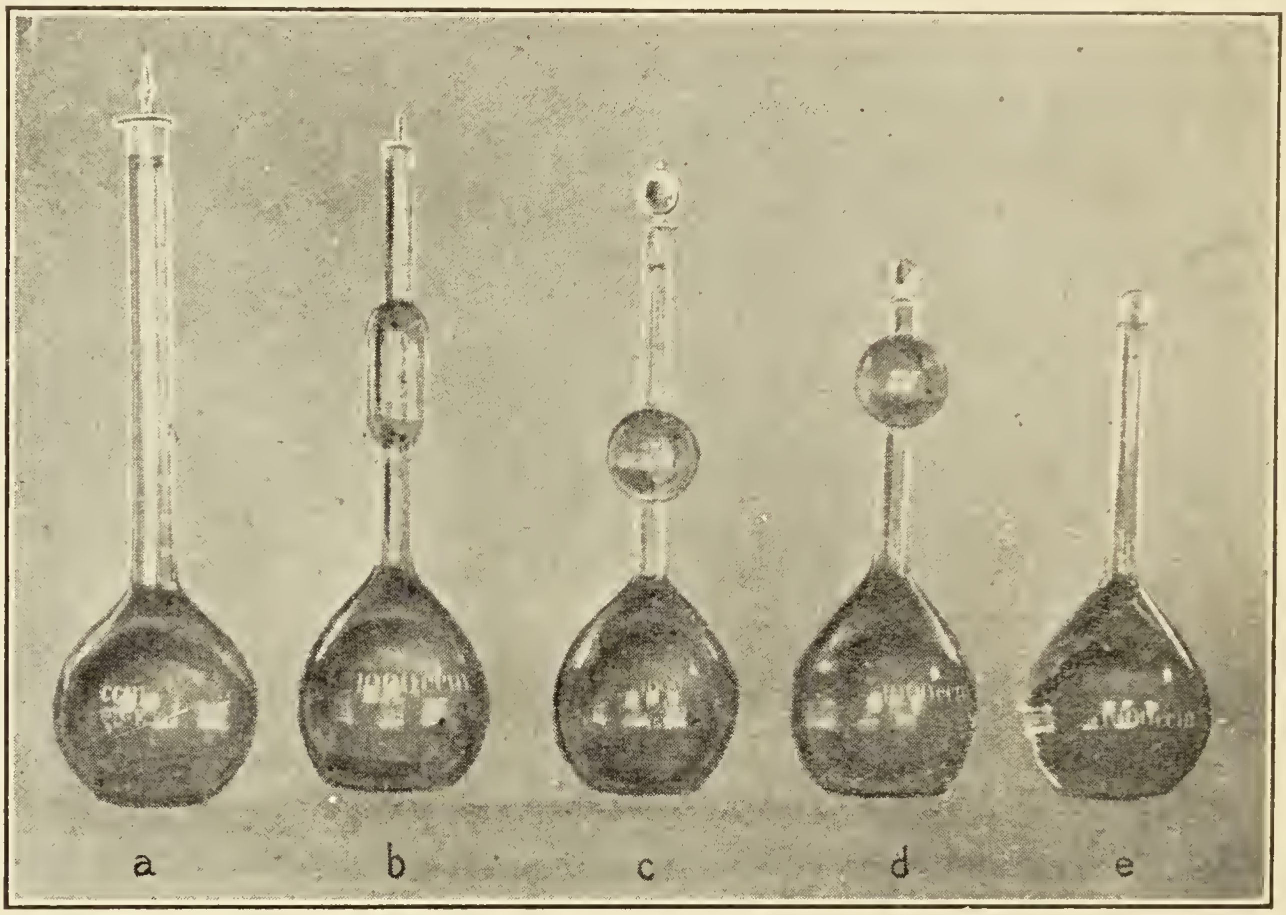

FIG. 22.—Standard flasks.

First weighing of beaker and spar	21·6327 grms
Second weighing of beaker and spar	21·1016 grms.
Iceland spar dissolved	0·5311 grms.

Since the molecular weight of Iceland spar is 100 (more exactly 100·07), and

$$2HCl + CaCO_3 \rightarrow CaCl_2 + 2H_2O,$$

it follows that 1 litre of normal acid will dissolve 50 grms. of the Iceland spar, or 20 c.c. will dissolve 1 gram. Had the acid been exactly half normal, 0·5 grm. of the spar would have dissolved.[2] The acid we have prepared is too concentrated. Pipette acid from the Giles' flask until the level of the liquid is at the 1000-c.c. mark. From the proportion — $0·5311 : 0·5 = 20 : x$, where

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[1] If ordinary flasks are used—figs. 22*d* or 22*e*—the volume withdrawn for testing, etc., should be noted, so as to avoid the use of measuring cylinders later on when the solution is diluted.

[2] It is here assumed that 100 is the molecular weight of the Iceland spar. If 100·07 be taken, the corresponding change must be made in the other numbers.

x = 18·83 c.c. It follows, therefore, in order to make the acid exactly half normal, 18·83 c.c. must be made up to 20 c.c., or 18·83 c.c. must be diluted with 1·17 c.c. of water. Hence, the 1000 c.c. now in the Giles' flask must be diluted with 62 c.c. of water in order to make the solution exactly half normal. The accuracy of the dilution should be established by repeating the experiment with the Iceland spar.[1] The most important source of error in this method of standardising the hydrochloric acid arises from the fact that the reaction is somewhat tardy towards the end, hence there is a danger of stopping before the reaction between the acid and spar is completed.

The advantages of hydrochloric acid as the standard acid for general work are: (1) it forms readily soluble salts with the alkalies and the alkaline earths (hence preferable to sulphuric and oxalic acids); (2) it is easily obtained pure (nitric acid often contains a little nitrous acid); (3) the strength of the acid is easily verified by means of silver nitrate; (4) the dilute solutions employed suffer no perceptible loss when boiled. For instance, a $\frac{1}{5}$N-solution boiled 10 minutes did not colour blue litmus paper held in the vapour, hence the steam which passes off is almost free from hydrochloric acid. (5) The strength of the acid does not change on keeping.

§ 23. Temperature Correction for Solutions of Hydrochloric Acid.

It has been assumed that the temperature of the acid solution did not differ more than 3° from the standard temperature, 15°. If the actual temperature deviates appreciably from this number, a correction must be applied in order to obtain the strength the acid would be at the standard temperature. The following correction table—Table XI.—is to be used in accurate work when allowance is to be made for variations of temperature of a normal solution of hydrochloric acid at a temperature different from that at which the substance was standardised, namely, 15°.[2] For solutions more dilute than one-tenth normal the correction table, page 29, for water may be employed.

Table XI.—Temperature Correction for N-HCl Solutions.
(Standard temperature, 15°.)

Temp.	0	1	2	3	4	5	6	7	8	9
0	...	...	...	...	...	+1·3	+1·2	+1·1	+1·0	+0·9
1	+0·8	+0·7	+0·5	+0·3	+0·2	Unit.	-0·2	-0·4	-0·6	-0·8
2	-1·1	-1·3	-1·5	-1·8	-2·1	-2·3	-2·5	-2·8	-3·1	-3·4

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[1] It should be remembered that in diluting the more concentrated solutions of salts, acids, etc., a change of volume may occur such that the volume of the mixture is less or greater than the sum of the separate volumes of the two components. The effect is seldom appreciable with dilute solutions, but with more concentrated solutions the effect may be serious if the dilution be not checked. Thus, with a solution of ammonium sulphate containing 56 grms. per 100 c.c., the contraction was found to be:

Ammonium sulphate taken	50·0	25·0	12·5 c.c.
Water taken	50·0	75·0	87·5 c.c.
Volume of resulting solution	98·83	99·64	99·89 c.c.

Changes of temperature on mixing sometimes cause a temporary expansion. Sufficient time must be allowed for the mixture to assume the temperature of the room before measuring liquid or the control experiment.

[2] The table also applies for N-oxalic acid. It is based on A. Schulze (*Zeit. anal. Chem.* **21.** 167, 1882). The table can be readily transposed into any other standard temperature different from 15°, as indicated on page 29.

Examples.—(1) 21·30 c.c. of $\frac{1}{10}$N-HCl have been used in a titration at 22°. The solution was standardised for 15°. The actual volume at 15° would be less than 21·30 c.c. From Table XI. the correction for 1 c.c. is $-0·0015$ c.c. Hence, $21·3 \times 0·0015 = 0·032$ c.c. or 21·30 c.c. at 22° corresponds with $21·30 - 0·03 = 21·27$ c.c. at 15°.

(2) A titration is made at 12°, and later on, at 20°. In the former case, 19·99 c.c. were employed, and in the latter case, 20·022 c.c. Suppose that no temperature correction be made, it follows that the two determinations give a difference of $100(20·022 - 19·99) \div 19·99 = 0·16$ per cent. As a matter of fact, both really correspond with 20 c.c. at the standard temperature, 15°.

These two examples give an idea of the error to which we are liable when the temperature is neglected. The temperature factors will be given for other solutions as occasion demands.

In order to facilitate the compounding of standard solutions at temperatures different from the standard, Heygendorff[1] has designed measuring flasks graduated for, say, 1000 c.c. at temperatures between 9° and 25°. These flasks resemble *a*, fig. 22.

§ 24. The Adjustment of Standard Solutions.

When large volumes of a solution are in question, the adjustment can be made without measuring the volume of the liquid litre by litre.[2] Suppose that 40–50 litres of a $\frac{1}{10}$N-soda solution are to be prepared. Make sufficient solution, about double the required strength, to about half fill the carboy in which the solution is to be stored. Pipette, say, three lots of 25 c.c. and titrate with $\frac{1}{10}$N-acid as indicated later on. Suppose that 25 c.c., as a mean of three titrations, require 31·25 c.c. of the standard acid. In that case, 80 c.c. of the given solution correspond with 100 c.c. of the $\frac{1}{10}$N-acid. This means that 250 c.c. of water must be added per litre of the solution in order to make it exactly $\frac{1}{10}$N. Now transfer, say, 200 c.c. of the solution into a 500-c.c. flask.

Add a litre of water to the solution ; stir ; withdraw, say, 200 c.c. for titration. Suppose that 8·33 c.c. now correspond with 100 c.c. of the $\frac{1}{10}$N-acid. The addition of the water has made a difference of 50 c.c. per litre in the amount of water needed to convert the given solution to the required strength. Hence, the carboy contained $1000 \div 50 = 20$ litres before the second sample was withdrawn for titration. The original solution required 250 c.c. of water per 1000 c.c. to make it exactly deci-normal. Hence, the original 20 litres will require

$$\frac{20 \times 250}{1000} = 5 \text{ litres}$$

of water in order to make it exactly deci-normal. But 1 litre has been added. Consequently, 4 more litres of water must be added.

A slight error is caused by withdrawing the 200 c.c. for the second trial. To correct this, dilute the 200 c.c. of the original solution standing in the 500-c.c. flask by adding 50 c.c. of water per litre; that is, 200 c.c. required 10 c.c. of water. The solution in the flask is the same strength as the 200 c.c. withdrawn for the second titration before adding the 4 litres of water. Hence, restore the 200 c.c. to the liquid in the carboy, and, if there has been no change of volume on mixing, the solution should be exactly decinormal, and occupy 25 litres.

Some prefer to leave the acid approximately half-normal, instead of adjusting the solution exactly, as described in the preceding section, by means of the Giles' flask. In that case, 20 c.c. of the acid are equivalent to 0·05311 grm. of calcium carbonate. But, from the above equation, 100 grms. of Iceland spar correspond with 79·936 grms. of hydrochloric acid, and therefore 0·5311 grm. of Iceland spar will correspond with $0·7294 \times 0·5311 = 0·3874$ grm. HCl. Hence, 20 c.c. of the acid has 0·3874 grm. of HCl; or 1 c.c. has 0·01937 grm. HCl. The bottle containing the solution may be labelled accordingly.

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[1] M. von Heygendorff, *Chem. Ztg.*, **35**. 382, 1911.

[2] F. M. Lyte, *Chem. News*, **26**. 159, 1872 ; **29**. 23, 1874 ; W. Smith, *ib.*, **30**. 220, 1869.

If but a small volume of acid is to be standardised, it may be advisable to follow the plan just described. In other cases a factor may be used. In the above example, the acid has 0·3874 grm. HCl per 20 c.c. If it were exactly normal, 20 c.c. would have 0·3647 grm. HCl. Or 18·83 c.c. is equivalent to 20 c.c. of half-normal acid; or the acid is 0·5311-normal when it should be 0·5-N. Dividing any pair of these numbers, say,

$$\frac{0·5}{0·5311} = 0·9415,$$

the resulting number—0·9415—represents the fraction of a cubic centimetre which is equivalent to 1 cubic centimetre of exactly $\frac{1}{2}$N-acid. Hence, in any given titration, the number of cubic centimetres multiplied by 0·9415 will give the number of cubic centimetres which would have been used with exactly $\frac{1}{2}$N-acid. Similarly, had 0·4311 grm. of spar been dissolved, the acid would have been too dilute, and the conversion factor would have been $0·5 \div 0·4311 = 1·16$.[1]

§ 25. The Adjustment of the Specific Gravity of Solutions.

Solutions of a definite specific gravity have sometimes to be made by diluting solutions of known specific gravity. The dilution is not usually required to be of very great accuracy.[2] When tables connecting specific gravity with concentration are available, the method can also be applied to the dilution of solutions of a given percentage composition to solutions of another percentage composition. In the absence of a knowledge of the law of contraction or expansion on dilution, the problem can only be solved approximately, because the methods of calculation assume that "the total volume of a mixture is equal to the sum of the volumes of its parts," and this assumption is not always justified. The following represent three typical cases :—

1. *It is required to prepare a volume* V *of a solution of specific gravity* S, *by diluting a volume* v *of a solution whose specific gravity is* s. Here V, S, and s are known, v is to be determined. It follows that $V - v$ will be the volume of the water needed, and we must have $vs + V - v = VS$. Hence, it follows

$$v = \frac{V(S-1)}{s-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[1] E. Petersen (*Zeit. anal. Chem.*, 45, 14, 439, 1906; G. Bruhns, *ib.*, 45. 204, 1906) recommends the adjustment of standard solutions by representing the approximately normal solution in terms of "equivalent volumes," that is, the number of cubic centimetres of the solutions which contain an equivalent weight of the substance in solution. Thus, in standardising hydrochloric acid, we have found 0·5311 grm. of Iceland spar to be equivalent to 20 c.c. of acid; hence, half of one equivalent of Iceland spar, namely, 25 grms., would be equivalent to half an equivalent of hydrochloric acid, and equivalent to 941·5 c.c. of the solution. Hence, the equivalent volume of the solution was 941·5 c.c.

[2] A. Vogel, *Deut. Illustr. Gewerbezeit.*, 202, 1865; C. D. Howard, *Journ. Amer. Chem. Soc.*, 19. 587, 1897. See almost any text-book on the elements of hydrostatics.

Example.—Soda lye of specific gravity 1·34 is to be diluted with water to make 50 c.c. of a solution of specific gravity 1·11. How much soda lye must be taken? Here, $V=50$ $S=1·11$, and $s=1·34$. Ansr. $v=16·18$ c.c.

2. *It is required to dilute a volume* v *of a solution of specific gravity* s, *so as to make a solution of specific gravity* S—*to find the amount of water needed.* Here, v, s, and S are known—to find V. When V has been determined, the required volume is given by $V-v$. From the preceding relation, we see that

$$V-v=\frac{v(s-S)}{S-1} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Example.—What volume of water is needed to reduce 50 c.c. of a solution of caustic soda of specific gravity 1·34 to a specific gravity 1·11? Here, $v=50$, $S=1·11$, $s=1·34$. Ansr. 154·55 c.c.

3. *It is required to dilute* v *c.c. of a solution of specific gravity* s *with another liquid of specific gravity* z *in order to get a solution of specific gravity* S—*to find what volume of liquid of specific gravity* z *is necessary for the purpose.* Here v, s, z, and S are known. Let u denote the required volume of the solution of specific gravity z, then

$$u=\frac{v(s-S)}{S-z} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Example.—50 c.c. of soda lye, specific gravity 1·34, is to be diluted with soda lye, specific gravity 1·11, in order to get a solution of specific gravity 1·2. What volume of the latter is needed? Here, $v=50$, $z=1·11$, $s=1·34$, $S=1·2$. Ansr. 77·8 − 50 c.c. = 27·8 c.c.

The problem of dilution is usually very easily solved by means of the specific gravity tables.

Example.—A solution of sulphuric acid, specific gravity 1·2, is to be prepared from the stock acid, specific gravity 1·84. From Table LXXV., 100 c.c. of acid, specific gravity 1·84, has 175·9 grms. H_2SO_4; 100 c.c. of an acid specific gravity 1·2 has 32·8 grms. H_2SO_4. If 100 c.c. of the concentrated acid has 175·9 grms. H_2SO_4, 18·64 c.c. will have 32·8 grms. of acid. Hence, if 18·64 c.c. of the concentrated acid be transferred to a 100-c.c. flask, and the solution made up to 100 c.c. (temperature constant), the result will be an acid of the desired concentration.

§ 26. The Calculations of Analytical Chemistry.

Slide Rule.—The slide rule is a convenient check on the accuracy of the arithmetic. Most of the calculations in general analytical chemistry are simple proportion. Simple proportion can be done very rapidly with the slide rule. For instance, take the proportion $2:3=4:x$. Place 2 on one scale over 3 on the other, and the value of x will be found over 4. Again, suppose a standard solution is such that 984 c.c. is equivalent to 1000 c.c. of a solution exactly normal; and 21·2 c.c. of the solution have been used in the titration. Set 984 on one scale over 1000 on the other scale, and the number of c.c. of an exactly normal solution will be found over 21·2. Again, what weight of SO_3 is equivalent to 0·321 grm. $BaSO_4$? Since 233 ($BaSO_4$) : 80·1 (SO_3) = 0·321 : x, set 80·1 over 233, and read the value of x over 0·321.

The regular slide rule of moderate length does not read to more than two figures, and a third by approximation, that is, approximately to the first decimal of one per cent. It is customary to write two decimals, in spite of the fact that the second figure is of no real value. Chemists have not therefore taken up the slide rule, owing to the uncertainty in the third and fourth figures. It is a general principle in chemical arithmetic that *the magnitude of the error due to* *the method of calculation must be well within the limits of the experimental error.* The ordinary slide rule does not satisfy this criterion. Hence, the chief function of the ordinary slide rule is to check the accuracy of calculations.[1] Errors which might escape detection by simply going over the figures may be thus revealed. G. Fuller's slide rule, however, is accurate enough for analytical requirements. It deals with four-figure numbers, and a fifth by an easy approximation. Its first cost (£3) is rather high, but it is *the* slide rule for chemical calculations.[2] I find it excellent.

Squared Paper.[3]—Let 1000 be taken as an abscissa on squared paper, and as ordinate lay off a length corresponding with the reduction factor of a given determination, say 736 for PbO in lead sulphate; 247 for chlorine in silver chloride, etc. Join, say, the ordinate 736 with the abscissa, then any particular weight of $PbSO_4$, found by analysis, is located on the abscissa axis, and the corresponding amount of PbO is read on the ordinate axis. This method is useful for *checking calculations*, and if the curve be drawn on a larger scale, it will be found as convenient as a table for saving time in analytical calculations.

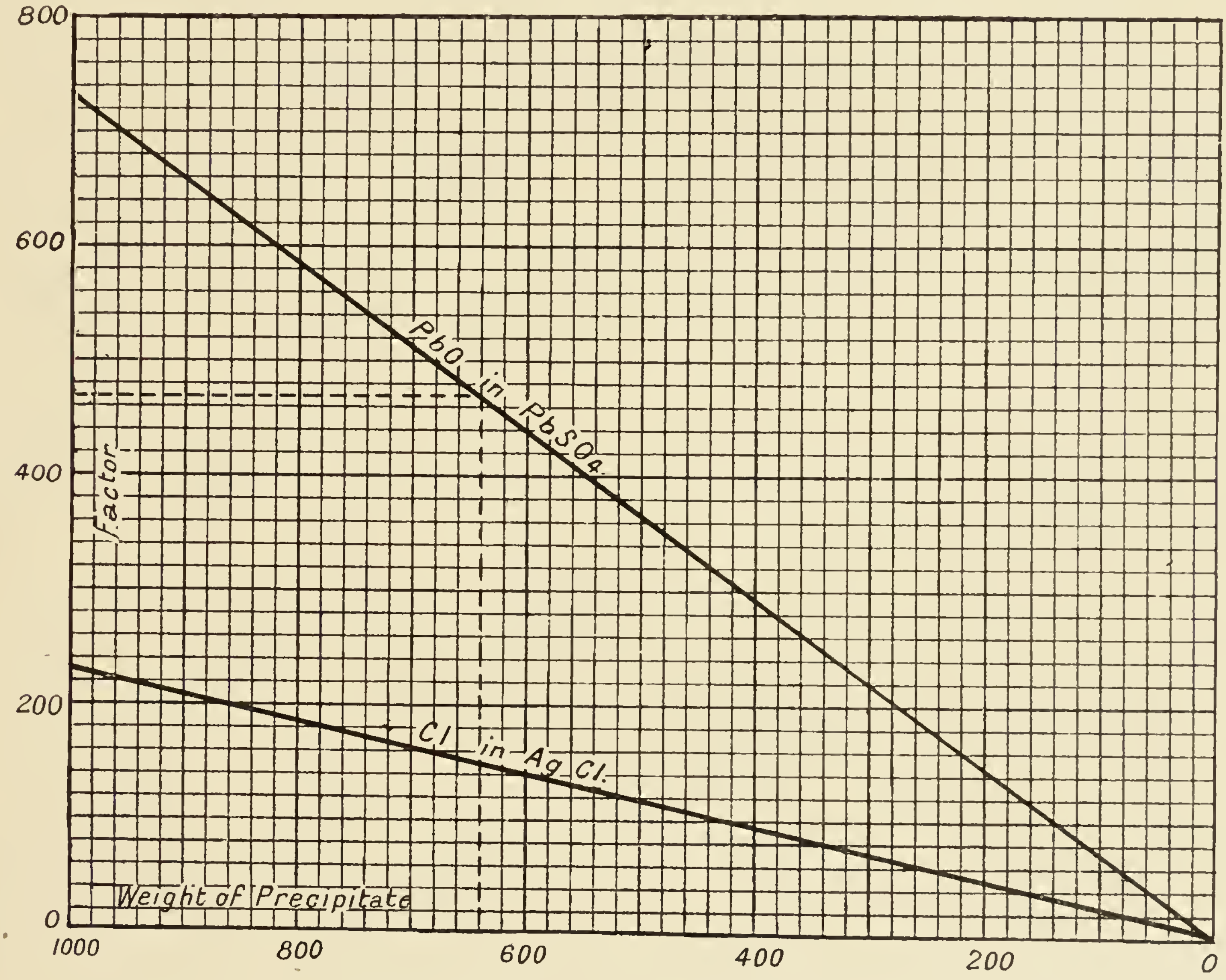

FIG. 23.—Charts to facilitate calculations.

EXAMPLE.—Suppose a precipitate of lead sulphate weighs 0·64 grm. The ordinate —fig. 23 (dotted lines)—corresponding with the abscissa 0·64 is 0·47; hence 0·47 grm. is the equivalent weight of PbO, corresponding with 0·64 grm. of $PbSO_4$.

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[1] "A. Nestler's slide rule for chemists" (D.R.G.M. 409844, 1910) is the ordinary type of slide rule with marks on the scale corresponding with some of the commoner factors used in certain analyses. The scale may be obtained from 25 to 50 cm. long, the price 10s. 6d. As a matter of fact, W. H. Wollaston invented a similar slide rule in 1814! W. H. Wollaston, *Phil. Trans.*, **104**. 1, 1814.

[2] A pamphlet explaining how the rule is used is sold with the instrument.

[3] F. P. Dunnington, *Journ. Amer. Chem. Soc.*, **25**. 537, 1903.

Analytical Tables.—Logarithms are in common use. Five-figure logarithmic tables suffice for the calculations in most analytical work.[1] In order to lessen the labour involved in calculating oft-repeated determinations, conversion tables may be used with advantage. This prevents wasting time and energy on a repetition of old operations, and conduces to more accurate work. Once accurate tables have been compiled, there is less liability to error. For instance, the amount of MgO in a given weight of magnesium pyrophosphate can be read from Table XC. at a glance; similar tables can be used for the amount of K_2O or KCl in a given weight of potassium chloroplatinate; PbO in $PbSO_4$; etc. Some of these tables are given in the Appendix.

Rational Weighing.—Another artifice for abbreviating calculations is to weigh an amount of substance for the analysis which bears a simple relation to the conversion factor.[2] *When the amount of substance taken for analysis is the same as the conversion factor, the weight of the precipitate directly corresponds with the percentage value sought*; and when the amount of substance taken for analysis is a simple multiple or sub-multiple of the conversion factor, the weight of the precipitate is a corresponding multiple or sub-multiple of the percentage value sought. For instance, if PbO is to be determined in a given substance, and if 0·7359 grm. of the sample be taken, then, if 0·5 grm. of lead sulphate be obtained, it follows that the sample contains 50 per cent. of PbO. It is easy to see this. Since 0·5 × 0·7359 grm. of PbO has been obtained from 0·7359 grm. of the sample, 100 grms. of the sample will have 50 grms. of PbO.

It must be remembered that time is lost in weighing a definite amount of a substance to such a degree of accuracy, and it is sometimes questionable if the time consumed in weighing is not greater than the time spent in solving the proportion, in this particular case:

$$\text{Weight of sample} : 0·7359 = \text{Weight of lead sulphate} : x.$$

At any rate, the risk of error, owing to the hygroscopic properties of fine powders, is sometimes greater in the former case. Similarly in volumetric work. A little thought spent in "designing" routine operations may save a great deal of work.

To find the relation between the weight of the sample to be taken for the analysis and the concentration of the standard solution employed so that the number of cubic centimetres of the standard solution may directly represent the percentage amount of the constituent sought.—The strength of the standard solution must be adjusted so that a weight w of the sample is equivalent to 100 c.c. In other words, 100 c.c. of the standard solution must be equivalent to a weight w of the (pure) constituent sought. For example, if 100 c.c. of the standard solution be equivalent to 3·942 grms. of the constituent under investigation, we must weigh exactly 3·942 grms. of the sample for the titration. In that case, if 41 c.c. of the standard solution be used in the titration, the sample contains 41 per cent. of the constituent in question.

EXAMPLE.—Suppose that it be required to determine the amount of sodium carbonate in a given sample of soda ash. For convenience, let $w=1$ grm. The standard acid solution must be so made that 100 c.c. contains the equivalent of 1 gram of sodium carbonate. By weighing 1 gram of the sample for each determination, every c.c. of the acid used in the titration will represent one per cent. of sodium carbonate in the sample.

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[1] For example, F. D. Küster, *Logarithmische Rechnentafeln für Chemiker*, Leipzig, 1910; C. J. Woodward, *Five-figure Logarithms for Chemists*, London, 1910.

[2] E. A. Uehling, *Journ. Anal. App. Chem.*, I. 402, 1887. E. B. and L. A. Voorkees (*ib.*, 7, 121, 1893) recommend specially graduated pipettes.

It may be advisable to use a more dilute solution. The strength of the standard solution can be made such that the percentage amount of the constituent sought in the given sample is one-tenth the number of cubic centimetres used in titration. Then, 1000 c.c. of the standard solution must be made equivalent to w grms. of the constituent (pure) under investigation.

Example.—Suppose that it be required to find the percentage amount of sodium chloride in a sample of soda ash. For convenience, let $w=2$. The standard solution of silver nitrate must be made such that 1000 c.c. corresponds with 2 grms. of sodium chloride. But 2 grms. of sodium chloride are equivalent to 5·81 grms. of silver nitrate. Hence, when the standard silver nitrate solution contains 5·81 grms. of silver nitrate per litre, and 2 grms. of the sample are taken, every 10 c.c. of the silver nitrate solution will represent one per cent. of sodium chloride in the given sample.

§ 27. The Automatic Filling of Burettes and Pipettes.

When titrations with a given solution have to be made at frequent intervals, one of the many[1] ingenious forms of burette available for automatic filling will save time. The four forms indicated below are typical, and useful in special cases, but there are scores of others. The chemist has here to consider a number of factors: convenience in filling, fragility, simplicity, first cost, repairs, etc. Is there a sufficient number of determinations to justify the installation? Automatic burettes may reduce the risk of error as well as save time and frequently also material.

Knöfler's Burette.—The burette shown in fig. 24 is a modification of Knöfler's. It is filled by opening the cock A, and forcing the liquid into the burette from the stock solution S by means of the rubber blower B. When the burette is full, close the cock A, and adjust the level of the liquid in the burette by means of the cock A or C. The burette is then used in the ordinary manner. If an excess of liquid remains in the burette, it can be run back into the main solution by opening the cock A. In Krawczynski's burette, there is a central tube passing from the cock A to the zero mark. The burette is graduated with this tube in position. If the burette should be filled above the zero mark, the excess runs back into the bottle when the blower stops. Hence the burette is automatically filled to the zero mark. There is then no provision for returning unused liquid to the main bulk. I prefer the burette without the central tube. The blower should have a tube packed with glass wool[2] to remove dust. The blower has a side tube to relieve the pressure when the blower stops. The side tube is kept closed while blowing.

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[1] O. Knöfler, *Chem. Ztg.*, **12.** 1142, 1888; A. Thilmany, *ib.*, **24.** 115, 1900; W. Fleming, *ib.*, **28.** 818, 1904; W. Schmidt, *ib.*, **28.** 154, 1904; S. Schiff, *ib.*, **14.** 233, 1890; A. Knauer, *ib.*, **9.** 231, 1884; A. Stein, *ib.*, **11.** 786, 1886; von der Heide, *ib.*, **35.** 568, 1911; F. Elsner, *ib.*, **7.** 1396, 1882; F. W. Dufert, *ib.*, **10.** 340, 1885; L. Hartmann, *ib.*, **8.** 418, 1883; H. R. Proctor, *ib.*, **16.** 1766, 1891; J. Stumpf, *ib.*, **14.** 441, 1889; A. Gawalovski, *Zeit. anal. Chem.*, **24.** 218, 1885; B. Pannertz, *ib.*, **45.** 751, 1906; V. Höbling, *ib.*, **28.** 431, 1889; A. Sauer, *ib.*, **14.** 311, 1875; D. Sidersky, *ib.*, **33.** 438, 1894; P. Metzyer, *ib.*, **39.** 791, 1900; F. Pannsetz, *ib.*, **45.** 750, 1906; F. Larssen, *ib.*, **26.** 333, 1887; R. Wollny, *ib.*, **24.** 406, 1885; E. Ducretet, *Zeit. Ver. Rubenzück. Ind.*, **22.** 49, 1889; K. Bourdon, *Dingler's Journ.*, **256.** 503, 1885; E. Greiner, *ib.*, **254.** 75, 1884; E. Waller, *Journ. Amer. Chem. Soc.*, **16.** 869, 1894; E. M. Johnson, *ib.*, **24.** 476, 1902; J. D. Rose, *ib.*, **32.** 703, 1910; E. S. Johnson, *ib.*, **19.** 281, 1897; J. L. Sammis, *ib.*, **21.** 42, 1899; E. R. Squibb, *ib.*, **16.** 145, 1894; G. A. Le Roy, *Monit. Scient.* (4), **6.** 719, 1892; A. M. Söderlund, *U.S. Pat. No.* 804894., 1905; R. König, *Brit. Pat. No.* 15160, 1905; C. J. van L. Hulsebock, *Pharm. Weekblad*, **43.** 1309, 1908; S. Krawczynski, *Ber.*, **26.** 3010, 1893; M. Guichard, *Bull. Soc. Chim.* (3), **11.** 4, 1894; E. Raymond, *Bull. Soc. Chim. Belg.*, **24.** 234, 1910; A. Chabaud, *ib.* (3), **31.** 349, 1904; R. Frailong, *Bull. Assoc. Chim. Sucr. Dist.*, **27.** 470, 1909; R. K. Meade, *The Design and Equipment of Small Chemical Laboratories*, Chicago, 37, 1908; F. Schubert, *Oester.-Ung. Zeit. Zuckerind. Landw.*, **36.** 629, 1907; F. Sestini, *Gaz. Chim. Ital.*, **7.** 225, 1875; G. Sire, *Ann. Chim. Phys.* (4), **28.** 108, 1873; C. S. Ellis, *Chem. News*, **81.** 29, 1900; E. French, *ib.*, **93.** 71, 1906; N. J. Lane, *Journ. Soc. Chem. Ind.*, **26.** 136, 1907.

[2] In the case of caustic solutions, a soda-lime tube is interposed to remove carbon dioxide.

Schiff's Burette.—Schiff's burette, fig. 25, has a bulb *S* connected with the burette by means of the two side tubes. The standard solution is poured into the main bulb. The burette is clamped vertically. To fill the burette, open the cock *A*. The liquid flows, by gravitation, into the burette. When full, close *A*. When the burette is empty, it can be refilled by opening *A* again. If necessary, the tube *B* can be connected with a soda-lime tube or hydrogen apparatus as indicated below. This burette is useful when a number of titrations have to be made at one time, but not necessarily at frequent intervals. It saves the necessity for frequently refilling the burette from the main solution. In Müller's modification[1] of Schiff's burette, the tubes about the bulb are eliminated, and a suitable stopcock is placed between the burette tube and the large bulb. It is therefore less fragile than Schiff's burette.

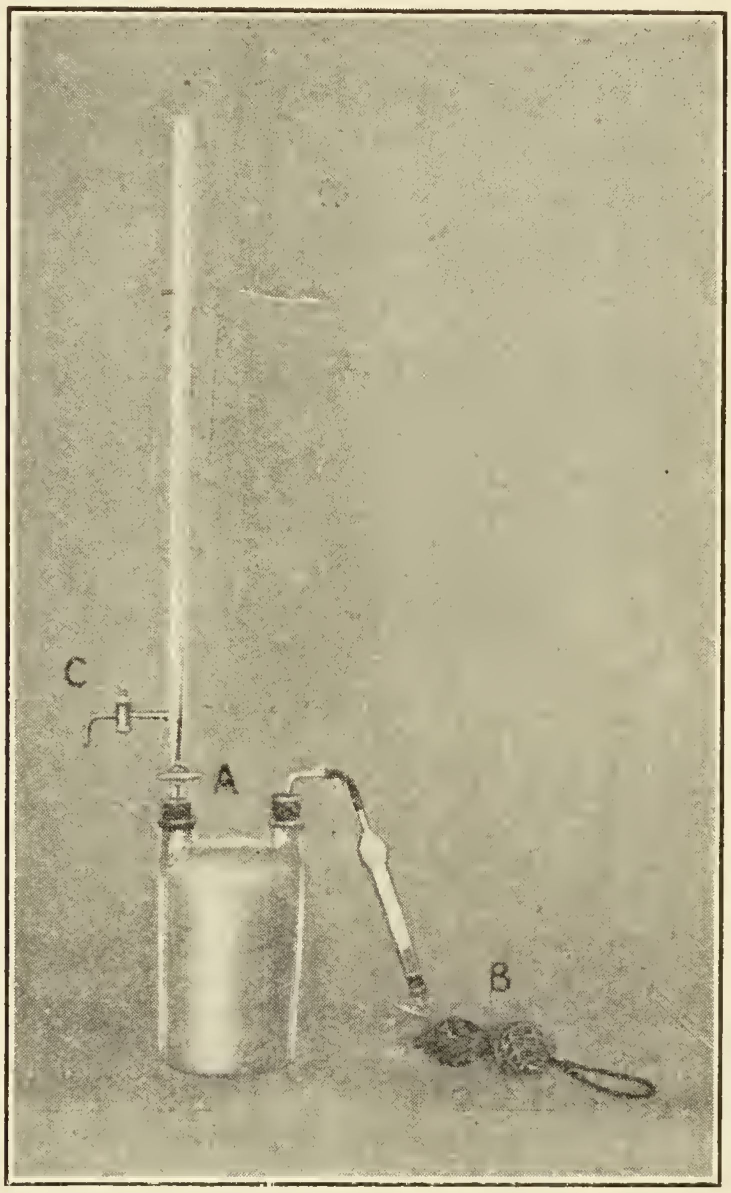

FIG. 24.—Knöfler's burette.

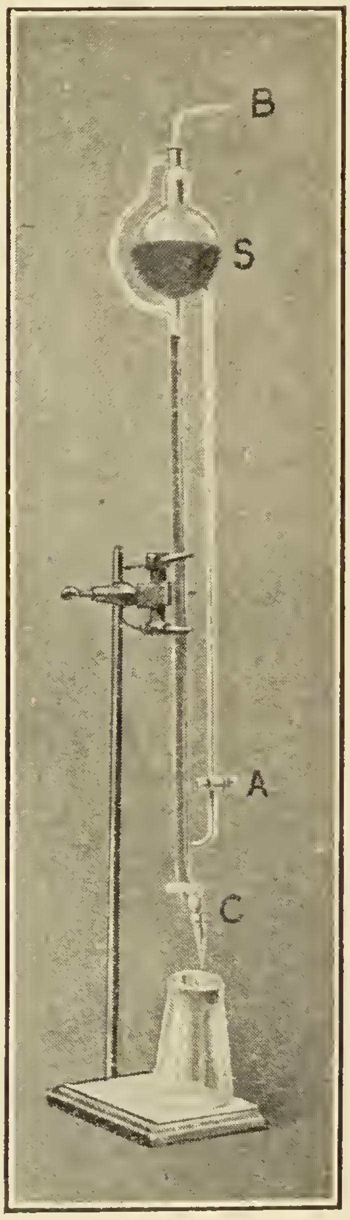

FIG. 25.—Schiff's burette.

Rammelsberg's Automatic Burette.—A favourite form of automatic burette is based upon fig. 26. This is a modification of Rammelsberg's. There are several other modifications in use. The stock solution can also be placed in a large carboy or bottles on a shelf. The liquid may either be syphoned from the stock solution into the burette, or run by gravity from a side tubulure (fig. 26) in the stock solution bottle *S*, by opening the glass stopcock or pinchcock at *A*. This form is used when larger volumes of standard solution are handled than is convenient with the forms indicated in figs. 24 and 25. If a standard caustic alkaline solution be in question, rubber plug cocks are employed. The diagram explains the method of constructing and using the apparatus. The method of charging will also be obvious. A T-tube is the best arrangement for connecting the burette with the bottle *S* and the atmosphere.

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[1] G. Müller (*Chem. Ztg.*, 32. 532, 1908) has a burette rather neater than Schiff's; and G. Müller and O. Berchem (*ib.*, 32. 711, 1908) a modification with a large reservoir.

Meade's Automatic Burette.—In Meade's modification (fig. 27) the stock solution is kept in, say, a Winchester under the bench. The burette is fitted with a three-way cock. To fill the burette, the cock is turned to connect the stock solution with the burette, and the blower is operated. When the burette is full, the cock is turned, and the level of the liquid in the burette is adjusted in the usual manner. The Winchester has a side opening to relieve the pressure; this is usually kept closed. By placing a two-hole rubber stopper at the top of the burette, and bringing the solution in at the top of the burette by means of a glass tube, instead of at the bottom, it is possible to automatically fill the burette to zero each time it is refilled, since any excess syphons back when the blower stops.

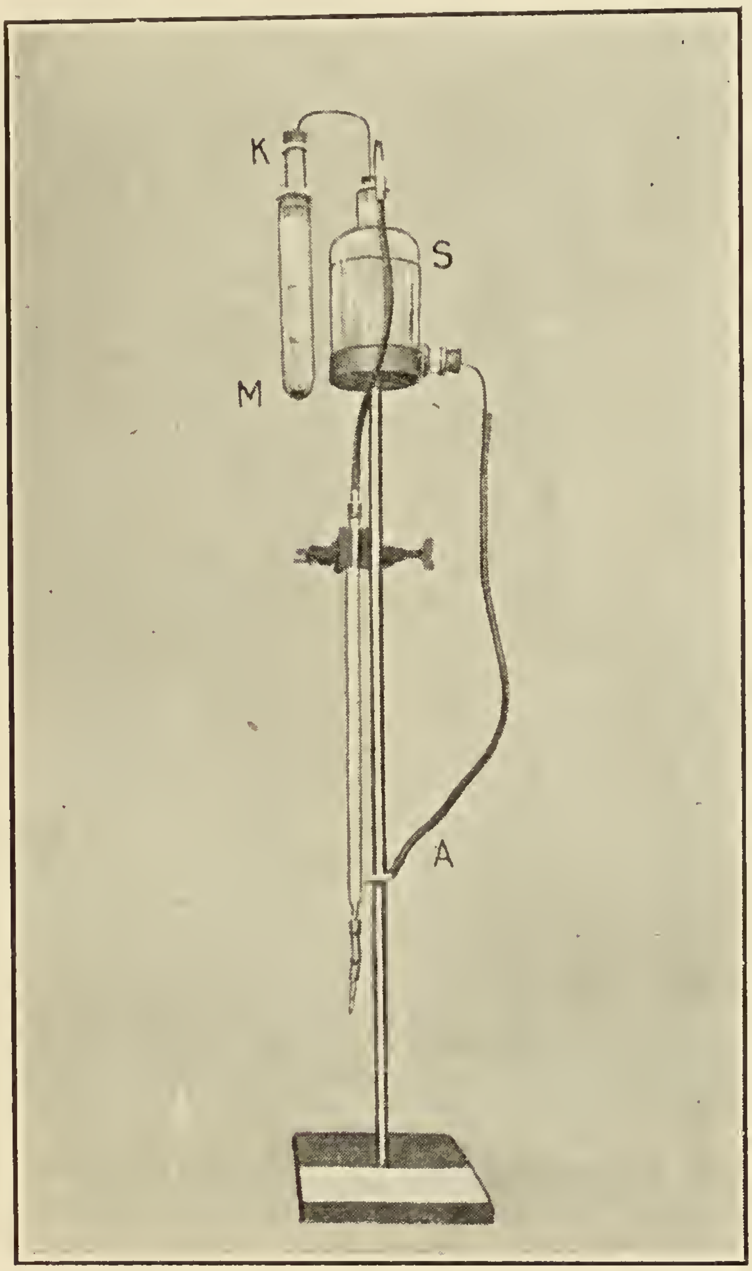

Fig. 26.—Rammelsberg's automatic burette.

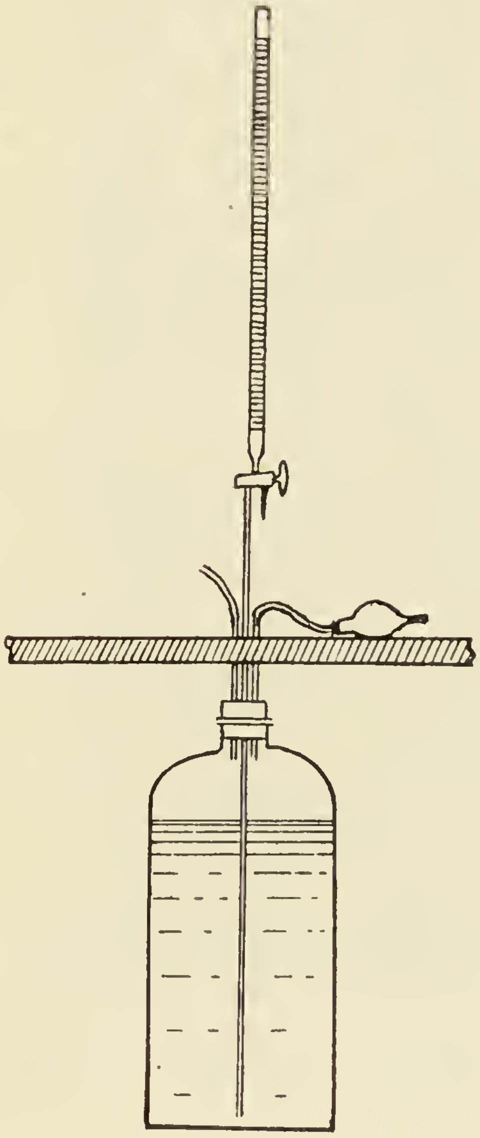

Fig. 27—Meade's automatic burette.

The last two types of automatic burettes are permanent fixtures. The burette is clamped to a suitable support. Owing to the fact that water evaporates and condenses in the upper part of a bottle, stock solutions should be shaken every day they are used.[1] Hence, rigid or fragile systems for storing stock solutions do not permit this agitation of the stock solution; accordingly, some object to the use of the forms indicated in fig. 27. Glass spiral springs are advantageously introduced where an apparatus is so rigid that it is liable to fracture with a jar or slight knock.

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[1] Some use vaseline oil to prevent evaporation.

Guard Tubes.—Standard solutions liable to absorb oxygen—stannous chloride, titanous chloride, etc.—can be kept in an atmosphere of hydrogen by connecting the air tube with a small apparatus for generating hydrogen whenever the pressure in the bottle is reduced below atmospheric.[1] This can easily be done by means of a perforated boiling-tube *K*—fig. 26—containing metallic zinc and an acid jar *M*. These are fitted together like many of the small hydrogen sulphide generators—*e.g.* Coram's or Johnson's. Mohr[2] recommended covering the solution with a layer of petroleum in order to prevent evaporation, oxidation, or the absorption of carbon dioxide by standard solutions of caustic alkalies, barium hydroxide, sulphites, etc. Morgan,[3] however, has shown that refined petroleum permits a comparatively rapid diffusion of oxygen from the air to the solution. The oxygen acts deleteriously on solutions of stannous chloride. He considers Sorge's suggestion to keep the bottle permanently connected with the coal-gas pipe is better than keeping a layer of petroleum over the surface of the solution.

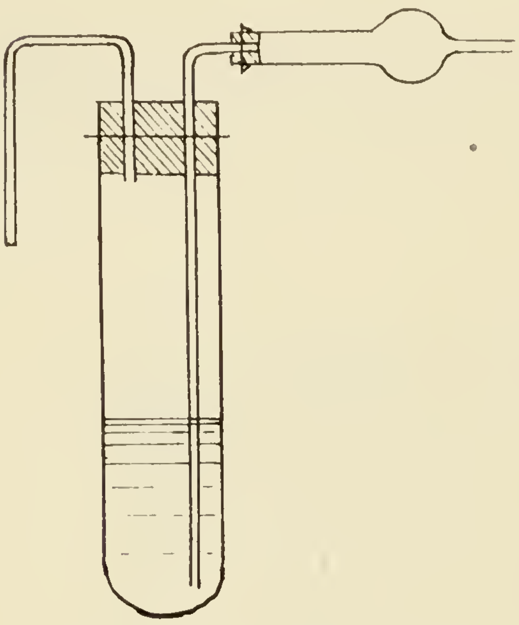
FIG. 28.—Blochmann's guard tubes.

With solutions of caustic alkalies and barium hydroxide, which rapidly absorb carbon dioxide from the air, the tube *E* should be connected with a U-tube containing soda-lime, so that all communication with the air must be made *viâ* this absorption tube. Blochmann's[4] arrangement (fig. 28) for this purpose is excellent. The tube *E* is connected with a test tube containing 5 to 10 c.c. of dilute (approximately $\frac{1}{50}$N) caustic potash coloured with a drop of phenolphthalein. The test tube is also connected with a soda-lime tube, as shown in the diagram. The test tube with the potash serves to indicate the efficiency of the soda-lime. Göckel's tube is rather neater (fig. 29). This may be attached both to the burette and to the stock solution, and charged with any desired solutions.

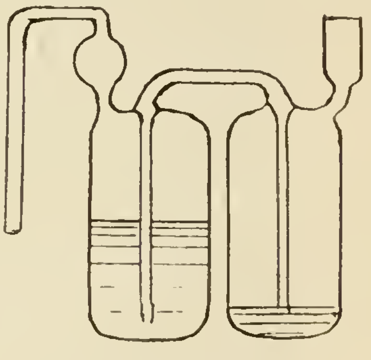
FIG. 29.—Göckel's guard tubes.

Revolver Pipettes.—When one and the same volume of a given liquid has to be frequently measured, overflow or "revolver" pipettes are convenient. There are many different forms.[1] Dupré's is illustrated in fig. 30. It can be made to deliver 25, 50, 100, or indeed any number of cubic centimetres. The three-way cock *A* connects the pipette with the stock solution. The rubber blower *B* forces liquid from the stock solution *S* to the pipette. When the pipette is full, the stopcock is closed, and the overflow runs back into the stock solution by opening the cock *P*. The pipette is then ready to deliver its liquid *viâ* the jet. A few moments' practice will show better how the instrument works than pages of descriptive matter. A tube with glass wool is interposed between the blower and the stock solution. The side tube is intended to relieve the pressure in *S* when the blower is stopped; it is closed when the blower is working.

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[1] A. Sauer, *Zeit. anal. Chem.*, **12**. 177, 1873 ; R. Fresenius, *Quantitative Chemical Analysis*, London, **1**. 226, 1876 ; R. H. Ridout, *Chem. News*, **29**. 3, 1874 ; G. S. Johnson, *ib.*, **57**. 213, 1888 ; H. C. Coram, *ib.*, **57**. 241, 1888 ; E. Douzard, *ib.*, **83**. 18, 47, 1901 ; Sorge, *Chem. Ztg.*, **5**. 145, 1880 ; E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, **47**. 1910 ; F. Resch, *Zeit. Oester. Apoth. Ver.*, **44**. 159, 1906 ; C. J. van Ledden Hulsebosch, *Pharm. Weekblad*, **43**. 1309, 1906 ; A. Scholl, *Zeit. Nahr. Genuss.*, **15**. 343, 1908 ; M. E. Pozzi-Escot, *Bull. Assoc. Chim. Sucr. Dist.*, **25**. 1077, 1908 ; von Heygendorff, *Pharm. Ztg.*, **54**. 159, 1909 ; S. Chumanoff, *Journ. Russ. Phys. Chem. Soc.*, **44**. 566, 1912 ; H. Mannhardt, *Journ. Amer. Chem. Soc.*, **27**. 299, 1905.

[2] F. Mohr, *Zeit. anal. Chem.*, 8. 113, 1869. C. Meineke and K. Schröder (*Zeit. öffent. Chem.*, **3**. 5, 1896) prefer vaseline oil. With permanganate solutions, a small amount of manganese peroxide separates out at first, but after standing a couple of months, the vaseline oil is said to have no appreciable effect on the strength of the solution. H. Mannhardt (*Journ. Amer. Chem. Soc.*, **27**. 299, 1905) recommends two wash-bottles, one with yellow phosphorus and the other with water, for cutting off oxygen from oxidisable solutions, *e.g.* $SnCl_2$.

[3] F. H. Morgan, *Journ. Anal. App. Chem.*, **2**. 164, 1888 ; B. Pawolleck, *Ber.*, **16**. 3008, 1883. S. Gneiwosz and A. Walfisez (*Zeit. phys. Chem.*, **1**. 70, 1887) have shown that the absorption coefficient of petroleum for oxygen is greater than that of water.

[4] R. Blochmann, *Liebig's Ann.*, **237**. 39, 1887 ; H. Göckel, *Chem. Ztg.*, **35**. 279, 1911 ; M. Lindt, *Met. Erz.*, **10**. 139, 1912.

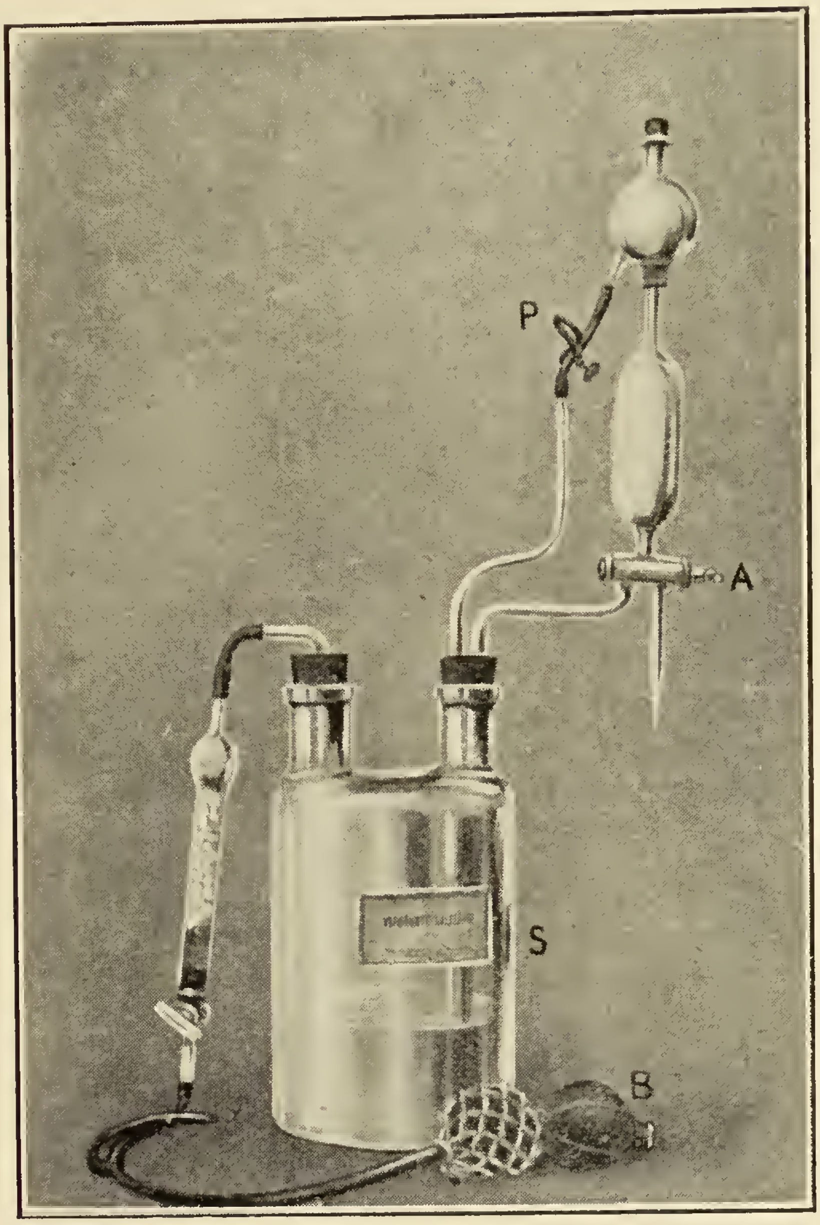

Fig. 30.—Dupré's revolver pipette.

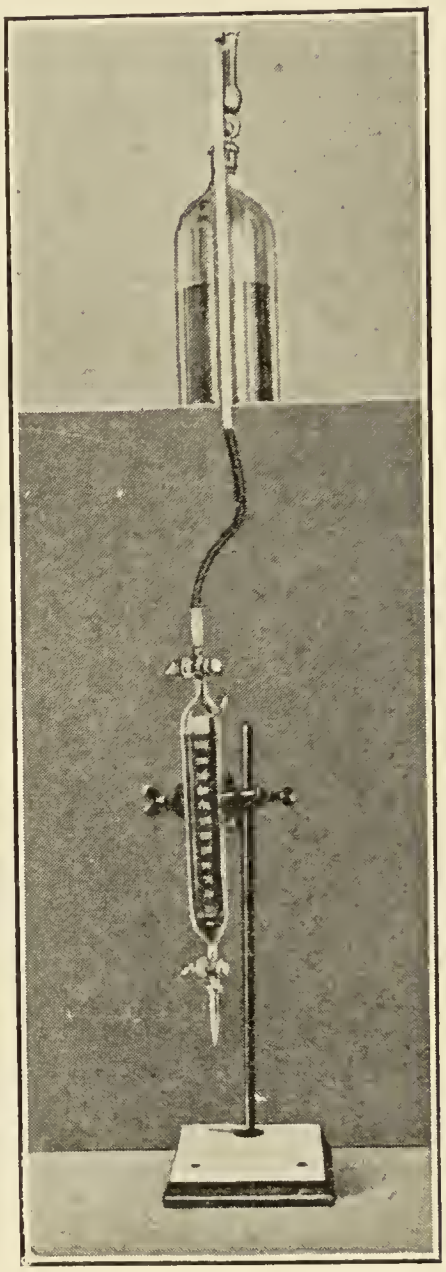

Fig. 31.—Measuring liquids.

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[1] R. Gerdes, *Chem. Ztg.*, **12.** 1109, 1888; C. Sander, *ib.*, **21.** 24, 1897; E. Strosehein, *ib.*, **13.** 660, 1890; G. P. Vanier, *Journ. Anal. App. Chem.*, **2.** 144, 1888; F. Soxhlet, *Rept. Anal. Chem.*, **6.** 637, 1886; F. Soxhlet and T. Henkel, *ib.*, **7.** 61, 1887; A. Beutell and F. W. Defeet, *ib.*, **7.** 186, 1887; E. L. Smith, *Journ. Amer. Chem. Soc.*, **18.** 905, 1896; F. G. Benediet, *ib.*, **31.** 652, 1909; A. Stutzer, *Zeit. angew. Chem.*, **7.** 309, 1895; J. Sebel, *Pharm. Centr.*, **36.** 156, 1896; E. Greiner and Friedrichs, *Zeit. anal. Chem*, **27.** 470, 1888; H. Seger and E. Cramer, *Tonind. Ztg.*, **19.** 580, 1895. For pipettes for sucking poisonous or fuming liquids, see E. Greiner, *Journ. Amer. Chem. Soc.*, **16.** 643, 1894; F. F. Skinner, *Chem. News*, **71.** 217, 1895; A. F. Reid, *ib.*, **66.** 166, 1892; A. Simon, *Archiv Pharm.* (4), **2.** 155, 1886; A. Meyer, *ib.* (3), **20.** 524, 1882; B. M. Mukerjee, *Chem. News*, **89.** 161, 1904; W. Hirschel, *Chem. Ztg.*, **28.** 359, 1904; B. Tolmaez, *Zeit. angew. Chem.*, **21.** 2551, 1908.

Measuring Glass.—Where different volumes of a liquid have to be frequently measured, and great accuracy is not needed, it is convenient to arrange[1] the liquid as shown in fig. 31. The measuring glass and general arrangement need no further description. The capacity of the measuring glass depends on the special circumstances.

§ 28. Indicators.

A large variety of indicators are available for volumetric analysis, but here only a limited number will be discussed.[2] The light is an important matter in volumetric work. A window facing the north is best. The colour changes of indicators often appear different when examined in gaslight. To one accustomed to work in daylight, the "transition tints" of some indicators may be misleading when viewed in yellowish artificial light. Incandescent and electric light are not very different from daylight. Direct sunlight is objectionable. It is generally best to use an Erlenmeyer's flask over a white tile, or sheet of white paper. It is often an advantage to work with two vessels the same size as the vessel in which the titration is to be made. Each contains about the same volume of liquid and the same amount of indicator as the vessel containing the solution under investigation. In one, the colour change has been effected. The two vessels, one containing the changed and the other the unchanged indicator, are useful for comparison until the eye has become accustomed to the tints of the indicator. It is sometimes advisable, in cases of uncertainty, to read the burette; if the addition of another drop of the standard solution alters the intensity but not the tint of the indicator, it is not included in the titration. In some cases the titration is continued until the change of tint is quite certain, and then titrate back with the proper standard solution to determine the exact end point.

1. *Litmus.*—Litmus is sold in the form of cakes, cubes, or granules. It is one of the oldest indicators, and even yet it is perhaps more frequently employed than any other indicator. An aqueous solution of litmus is blue in the presence of a slight excess of alkalies or alkaline earths; the solution is coloured red in the presence of a slight excess of acid. The neutral solution is violet. The instability of its aqueous solution is the main objection to litmus. The solution does not keep very well.[3] The sensitiveness of the solution prepared by digesting commercial litmus in water is not the best possible, since the litmus contains at least two distinct colouring principles—one a very sensitive violet colour, and the other a red colour of feeble sensitiveness. The latter obscures the tints of the violet principle. Püschel[4] isolates the violet colouring principle in the following manner:—

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[1] E. S. Johnson, *Journ. Amer. Chem. Soc.*, 19. 281, 1897. For a combined measuring pipette and wash-bottle, J. W. Hogarth, *Journ. Roy. Soc. N.S.W.*, 38. 418, 1905; *Chem. News*, 93. 71, 1906; J. Hudig and M. J. van't Kruys, *Chem. Weekblad*, 7. 879, 1910; T. O. Smith, *Journ. Ind. Eng. Chem.*, 4. 47, 1912.

[2] F. Glaser, *Indikatoren der Acidimetrie und Alkalimetrie*, Wiesbaden, 1901; A. I. Cohn, *Indicators and Test-papers*, New York, 1899, deal with those proposed up to their time of publication. For the theory of indicators, see the text-books on physical chemistry, or J. W. Mellor, *Chemical Statics and Dynamics*, London, 214, 1904; E. Salm, *Zeit. Elektrochem.*, 10. 341, 1904; 12. 99, 1906; *Zeit. phys. Chem.*, 57. 471, 1906; E. Salm and H. Friedenthal, *Zeit. Elektrochem.*, 13. 125, 1907.

[3] The commercial article contains a gelatinous substance which acts as a good medium for the growth of fungi and bacteria. R. Dubois, *Bull. Soc. Chim.* (2), 49. 763, 1888; A. Vogel, *Journ. Pharm. Chim.*, 45. 70. 1864; *Chem. News*, 9. 205, 1864; B. Balli, *Chem. Ztg.*, 15. 68, 1191, 1896. If sterilised, the solution does not change so readily. Phenol, thymol, and chloroform have been recommended for this purpose.

[4] A. Püschel, *Oester. Chem. Ztg.*, 13. 185, 1910; M. Kretzschimar, *Chem. Ztg.*, 3. 682, 1879; K. Mays, *Chem. Centr.* (3), 17. 99, 1886; V. de Luynes, *Chem. News*, 11. 149, 1865;

Digest 100 grms. of commercial litmus with 600 c.c. of hot distilled water, and after allowing the mixture to stand for some time, decant the solution from the sediment.[1] After standing a few more days, the solution is again decanted from any sediment. Evaporate the solution in a porcelain basin (400 c.c.) down to about 200 or 250 c.c. Filter the solution while hot into a half-litre flask. Make the filtrate up to about 300 c.c. with distilled water. Mix 50 c.c. of distilled water with 16 grms. of pure concentrated sulphuric acid in a separate flask, and make the solution up to about 100 c.c. Mix the two solutions, and digest the mixture on a water bath, with frequent agitation, for about 4 hours. A dark brownish-red gelatinous precipitate gradually separates.[2] When cold, filter through a 12·5-cm. filter paper.[3] Wash the precipitate with cold distilled water until the washings give no sulphuric acid reaction with barium chloride. The precipitate still contains some of the red colouring principle and the gelatinous matters. The washing is therefore continued in order to remove the former. The wash-water has a faint red colour which gives a violet colour with potash solutions as long as the red colouring principle remains. When the wash-water gives a dark blue colour with potash,[4] it is supposed that nearly all the red colouring matter is washed away. The precipitate is then digested in dilute alcohol by pouring 100 c.c. of warm 90 per cent. alcohol, in small quantities at a time, through the filter paper. The colouring principle passes into solution, the gelatinous matter remains behind. Collect the washings in a porcelain basin. Add a drop of ammonia to the later portions of alcohol which are passed through the paper. Finish the washing with pure alcohol. Evaporate the solution to dryness on a water bath. Dissolve the residue in hot distilled water. Filter. Make the solution up to 600 c.c. Divide the red solution into approximately two equal portions. Neutralise the one portion with a dilute solution of caustic potash. The solution then becomes blue. Mix the two solutions. Again divide the solution into two portions, and repeat the operation until the solution has a neutral violet tint.[5] This solution does not change on keeping in glass-stoppered bottles.[6]

Litmus solution is quite satisfactory for the titration of caustic alkalies, alkaline earths, and ammonia; also for hydrochloric, sulphuric, nitric, and oxalic acids. It can only be used with carbonates or bicarbonates when the liberated carbon dioxide is driven off by boiling the solution. The dissolved gas in cold solutions causes the red colour to persist even when the titration is completed. Hence, although quite satisfactory in *boiling* solutions of the carbonates, litmus should not be used with *cold* solutions. Similar remarks apply to the sulphides. Litmus can also be used for titrating arsenites and silicates, but not for titrating

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V. Wartha, *Ber.*, **9.** 217, 1876; B. Reinitzer, *Zeit. angew. Chem.*, **7.** 547, 1894; O. Förster, *Zeit. anal. Chem.*, **28.** 428, 1889; P. Scheitz, *ib.*, **49.** 735, 736, 1910; W. Schäfer, *Apoth. Ztg.*, **9.** 839, 1894; E. W. Rice, *Journ. Ind. Eng. Chem.*, **4.** 229, 1912.

[1] The solution will take no harm if the temperature be kept below about 6°. The bacteria grow only at higher temperatures than this. Hence, this work is best done during the winter months.

[2] Presumably a sulpho-salt of the violet colouring matter.

[3] No. 575, C. Schleicher and Schüll's filter paper.

[4] A sensitive eye can tell when the washing is finished by the fiery red tint of the washings.

[5] A neutral solution appears violet by transmitted light. It is coloured red by a trace of acid, and blue by a trace of alkali.

[6] Litmus paper is made by coating one side of a sheet of pure white paper with a solution of one part isinglass in 50 c.c. of water. When dry, coat the isinglass with the litmus solution. A. Vacher, *Chem. News*, **17.** 277, 1868; F. Mohr, *Zeit. anal. Chem.*, **12.** 368, 372, 1893. The "*dupli-test litmus papers*," with a strip of blue and of red litmus separated by a thin strip of cerasine or paraffin, are most convenient for finding if a solution is "acid" or "alkaline." They are made by Die Chemische Fabrik Helfenberg—K. Dietrich, *Zeit. angew. Chem.*, **14.** 1091, 1904.

sulphurous, phosphoric, arsenic, boric, and chromic acids. It is also useless for titrating most organic acids, *e.g.* tartaric and citric acids.

2. *Phenolphthalein.*—The solution of phenolphthalein is made by dissolving 5 grms. of phenolphthalein in 500 c.c. of absolute alcohol, and making the solution up to a litre with water. Use about 1 c.c. for each titration.

Phenolphthalein solution is nearly colourless in neutral and acid solutions, but red in the presence of a slight excess of alkali. It is used in titrating the hydroxides of the alkalies and alkaline earths; the mineral acids; and most organic acids. It does not work satisfactorily in the presence of ammonia, ammonium salts, and alcohol; nor does it give satisfactory results with arsenious, silicic, and boric acids. It is very sensitive to carbonic acid, and hydrogen sulphide, but it appears neutral when the acid salts have been formed. Hence, phenolphthalein may be employed to detect sodium carbonate in the presence of sodium bicarbonate. It also appears neutral with arsenic and phosphoric acids when two-thirds of the hydrogen has been replaced.[1]

3. *Methyl Orange.*—The solution is prepared by dissolving 1 grm. of methyl orange in a litre of water.

The solution is orange yellow in neutral or alkaline solutions, and it changes to pink with a slight excess of acid. The end point with methyl orange is not so sharp as with phenolphthalein, since methyl orange shows several shades of colour—"transition tints." This trouble, however, is aggravated by the use of too much indicator. Two drops of the above solution are sufficient to impart a distinct yellow to a solution.[2] If the colour fades during a titration, add another drop of the indicator.

Methyl orange is not so suitable for titrations in the presence of methyl alcohol as *p*-nitrophenol. Methyl orange is almost wholly indifferent to the presence of carbon dioxide, and less so than nitrophenol. It is also practically indifferent towards aqueous solutions of hydrogen sulphide, arsenious, boric, silicic, and hydrocyanic acids. It can therefore be used for the strong mineral acids, hydroxides of the alkalies and alkaline earths; ammonia; carbonates, sulphides, arsenites, silicates, and borates which are decomposed by dilute nitric, hydrochloric, or sulphuric acids. Phosphoric and arsenic acids become neutral to this indicator when one-third of their replaceable hydrogen has reacted with the alkali; and sulphurous acid becomes neutral when the acid sulphite is formed. Methyl orange is not to be used for the organic acids. Solutions containing nitrous acid or nitrites destroy the colour. It must be used in cold, not hot, solutions, since the end point becomes indistinct and loses its sharpness when titrations are made in hot solutions. If it be desired to eliminate the slight effect of carbon dioxide on methyl orange in titrating the carbonates, the solutions may be boiled when nearly neutralised, and the titration finished when the solution is cold.

4. *p-Nitrophenol.*—A solution of *p*-nitrophenol is made by dissolving 1 grm. of *p*-nitrophenol in 75 c.c. of absolute alcohol, and making the solution up to 1 litre, that is, 1000 c.c., with water.[3]

p-Nitrophenol is yellow in alkaline solution, and colourless in neutral or acid solutions. It is rather more sensitive to carbon dioxide than methyl orange. The first appearance or disappearance of the yellow colour during a titration is so gradual that it requires a sensitive eye in daylight to recognise the change accurately. Hence, methyl orange is preferable to *p*-nitrophenol in most cases. *p*-Nitrophenol is somewhat sensitive to boric acid in the presence of glycerol or mannitol, but not very sensitive to boric acid without these auxiliaries.[1]

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[1] H. N. and C. Draper, *Chem. News*, **55**. 133, 143, 1887; J. H. Long, *ib.*, **51**. 160, 1885.

[2] R. T. Thomson (*vide infra*) recommends a solution containing 0·15 grm. per litre, and uses 0·5 c.c. of this solution per 100 c.c. of the solution to be titrated.

[3] L. Spiegel, *Ber.*, **33**. 2640, 1900; *Zeit. angew. Chem.*, **17**. 715, 1903; G. Lunge, *ib.*, **16**. 560, 1903; **17**. 202, 1904; A. Goldberg and K. Naumann, *ib.*, **16**. 644, 1903; H. W. Langbeck, *Zeit. anal. Chem.*, **21**. 100, 1882.

Hildebrandt[2] summarises what he calls the "usability" of a number of indicators in the form of a table, from which Table XII. has been taken:—

Table XII.—Conditions under which Indicators can be best used (Hildebrandt).

Indicator.	Titration.				Ammonia and NH_4Cl.	In presence of sodium acetate.
	Cold.	Hot.	Alkali to acid.	Acid to alkali.		
1. Litmus . .	Usable only on exclusion of CO_2	Usable	Usable only on exclusion of CO_2	Usable only on exclusion of CO_2	Usable	Not usable.
2. Phenolphthalein	Usable on exclusion of CO_2	Usable	Usable	Usable	Not usable	Usable.
3. Methyl orange .	Usable for N- and $\frac{1}{10}$N-Na_2CO_3 with N- and $\frac{1}{10}$N-HCl and $Ba(OH)_2$ solutions	Usable	Usable	Usable for baryta; for N-Na_2CO_3 only if hot	Usable	Not usable.
4. *p*-Nitrophenol .	Usable except with N-Na_2CO_3	Not usable	Usable	Usable only for baryta and hot N-Na_2CO_3	Usable	Not usable.

5. *Cochineal.*—This substance occurs in commerce in the form of rounded grains which are the dried bodies of female hemiptera which lived on certain species of cacti. The so-called "silver cochineal" is the best. To prepare a solution, macerate 3 grms. of coarsely powered[3] cochineal in 250 c.c. of a mixture of 3 vols. of water, and 1 vol. of alcohol. Decant off the clear deep ruby red solution through a filter paper. The solution is coloured violet by alkalies, carbonates of the alkalies and alkaline earths, sodium phosphate, and salts of weak acids generally. Acids restore the yellowish-red colour. The indicator is less affected by carbon dioxide than litmus, and it gives better results when used in artificial light. It is useless for titrating organic acids. Salts of iron, aluminium, and copper yield a pink colour with this indicator, and hence these salts should be absent from the solution to be titrated.

6. *Phenacetolin.*—This substance occurs in commerce as a yellowish-brown powder. It is used as an indicator in aqueous or alcoholic solution. The aqueous solution is 1 : 500; the alcoholic solution 1 : 200. The green-coloured solution is turned yellow with acids and caustic alkalies, and red with carbonates

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[1] A. Goldberg aud K. Naumann, *Zeit. angew. Chem.*, **16.** 644, 1903.

[2] H. Hildebrandt, *Wochschr. Brauerei*, **22.** 69, 1906; R. T. Thomson's papers on the indicators should be studied. R. T. Thomson, *Chem. News*, **47.** 123, 184, 1883; **49.** 32, 119, 1884; **52.** 18, 29, 1885; A. H. Allen, *Analyst*, **17.** 186, 215, 1892.

[3] If finely powdered, the decoction is difficult to filter.

of the alkalies and alkaline earths, alkaline sulphides, and ammonia. It is therefore useful for estimating calcium hydroxide or calcium oxide in the presence of calcium carbonate; sodium hydroxide in the presence of sodium carbonate, etc., provided sufficient hydroxide be present, and ammonia be absent.[1] If an excess of the carbonate be present, the colour change is not well defined. It requires some practice to get reliable results. The titration is made by adding standard sulphuric or hydrochloric acid rapidly until the yellow colour is succeeded by a faint rose colour. All the caustic alkali is now neutralised, and the burette is read. Any further addition of acid intensifies the red colour until all the carbonate is decomposed, when the colour passes to a yellowish red, and finally yellow. The burette is read, and the results furnish data for calculating the amount of hydroxide and carbonate in the given sample.

It will not do to change indicators except for a specific reason. Working with $\frac{1}{100}$N-solutions of sodium hydroxide and hydrochloric acid, Scholtz[2] found that 10 c.c. of acid and alkali required respectively for neutralisation—

	Litmus.	Phenolphthalein.	Methyl orange.	*p*-Nitrophenol.	
10 c.c. alkali .	9·83	9·68	10·70	10·00	c.c. acid.
10 c.c. acid . .	9·92	10·08	9·28	9·99	c.c. alkali.

The inference is obvious: in using centi-normal solutions, the indicator, and the direction of the titration—acid to alkali or conversely—employed in standardisation should be the same as is used in the actual determination.

Indicators are conveniently kept in bottles fitted with a pipette, in order that the indicator may be removed without contact with the stain which usually collects about the necks of the bottles when the solutions are transferred in the ordinary manner. This stain interferes with the sharpness of the end point—*e.g.*, methyl orange in the bromate process for antimony. A nest of four pipette bottles for the most commonly used indicators is illustrated in fig. 32. The indicators, when kept in this way, are easily carried from bench to bench.

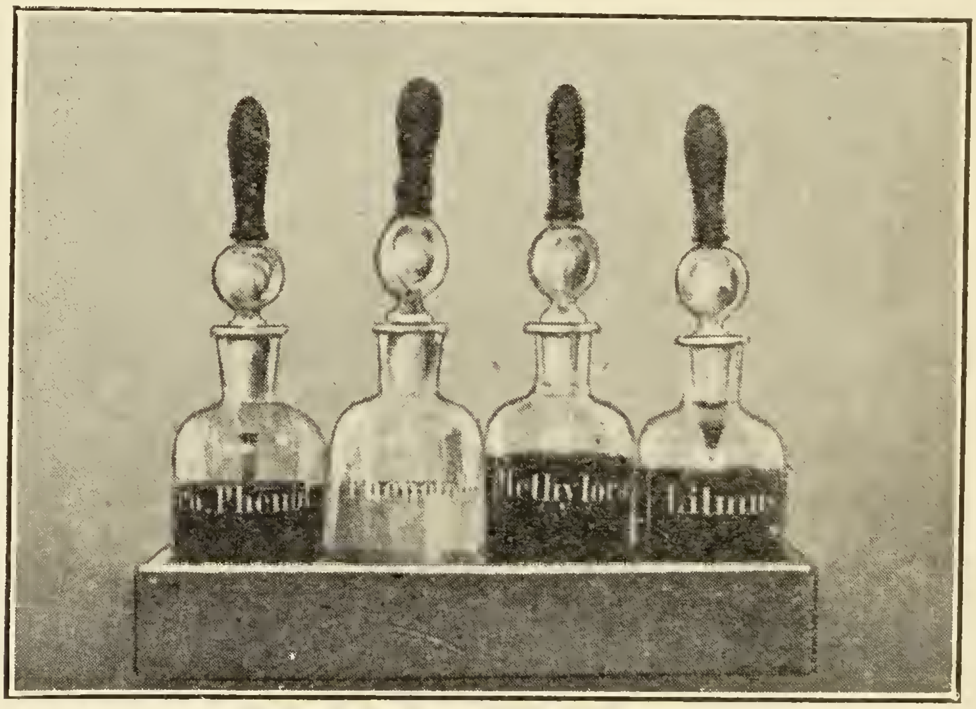

FIG. 32.—Nest of pipette bottles for indicators.

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[1] G. Lunge, *Chem. Ind.*, 4. 349, 1881; *Journ. Soc. Chem. Ind.*, I. 56, 1882. See page 72 for Winkler's barium carbonate process.

[2] M. Scholtz, *Arch. Pharm.*, 242. 575, 1904.

§ 29. Standard Solutions of Sodium Hydroxide.

Sodium hydroxide—NaOH. Molecular weight: 40·01; equivalent weight: 40·01.

The most commonly employed solutions are:—

	Grm. NaOH per c.c.
N-Sodium hydroxide	0·04001
½N-Sodium hydroxide	0·020005
⅕N-Sodium hydroxide	0·008002
$\frac{1}{10}$N-Sodium hydroxide	0·004001

Sodium hydroxide does not make an ideal standard solution, since it is liable to absorb carbon dioxide from the air.[1] A solution of sodium hydroxide is also particularly liable to attack glass, and to gradually lose its strength. In consequence, it is not usually advisable to make up a large stock of the solution. Küster recommends storing sodium hydroxide in the nickel bottles made by Krupp of Berndorf. Glass stoppers and glass stopcocks are also objectionable because they are liable to become immovably fixed. It is therefore advisable to use rubber stoppers and rubber plug cocks with the burettes working caustic lyes.

To prepare a half-normal solution of sodium hydroxide, select a number of clear sticks of sodium hydroxide, pure by alcohol. Scrape off the opaque parts; dissolve 27 grms. in water and make the solution up to 1100 c.c. in a Giles' flask. Recently boiled distilled water must be used in order to keep out the carbon dioxide. When the solution has attained a temperature of 15°, pipette 25 c.c. into an Erlenmeyer's flask;[2] add two or three drops of methyl orange solution as indicator; run acid from the burette until the yellow colour of the methyl orange changes to an orange colour. Read the burette. Continue the titration, drop by drop, until the addition of a single drop of acid turns the solution pink.[3] Again read the burette. Repeat the titration with two more portions of 25 c.c. Let 26·42 c.c. denote the mean volume of the acid used in the titration, then 25 c.c. of the sodium hydroxide solution contains an amount of alkali corresponding with 26·42 c.c. of ½N-acid. If the alkali be exactly ½N, like the acid, 25 c.c. of acid would have been used. Hence, 25 c.c. of alkali must be increased by 26·42 less 25 = 1·42 c.c., or 1000 c.c. by 56·8 c.c. of water. Hence, pipette alkali solution from the flask until the liquid stands at the 1000-c.c. mark, and add 56·8 c.c. of water in order that the alkali may be exactly half-normal. Verify the accuracy of the dilution by repeating the titration.

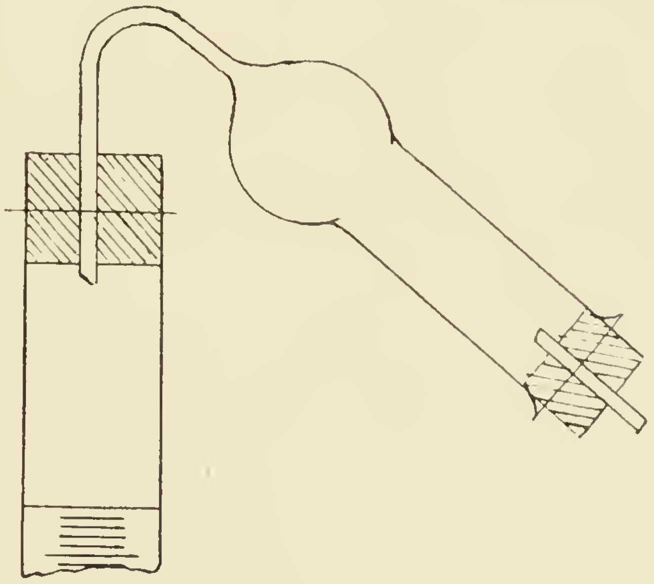

FIG. 33.—Burette with guard tube.

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[1] E. Fleischer (*Chem. News*, **19**. 203, 1869), in consequence, prefers a ½N-ammonia solution as a standard alkali. If solutions over this strength be used, they are liable to change, owing to the loss of ammonia; and even ½N-solutions are liable to lose ammonia on a hot summer's day, when the temperature is, say, 25°. There is also a difficulty with some of the indicators when ammonia solutions are used. R. Rempel, *Chem. Ztg.*, **9**. 1906, 1884; G. T. Gerlach, *Chem. Ind.*, **12**. 97, 1889.

[2] The liquid should be thoroughly agitated during the titration. An Erlenmeyer's flask is generally preferable to ordinary narrow-necked flasks, to beaker and glass rod, or to basin and glass rod, because its contents are so accessible, and so easily agitated without stirring.

[3] At first, it is best to work with comparison flasks, as described page 60.

In the case of boric oxide titrations special care must be taken to exclude carbon dioxide. The burette and stock solution should be well protected from atmospheric carbon dioxide. The burette may be mounted as described in figs. 24 and 27; or, for small quantities, a soda-lime[1] tube may be fitted to the top of the burette as indicated in fig. 33. To test if the solution is really free from carbonates, make two parallel titrations with phenolphthalein as indicator. If the one solution be hot, and the other cold, carbonates will be absent if the two results agree. If otherwise, carbonates are present.

Küster's Process.—In special cases Küster's method[2] of preparation may be used. Boil distilled water in a vessel through which the air is aspirated. The air is freed from carbon dioxide by passing it through a potash wash-bottle, and through soda-lime. This removes any carbon dioxide which would be dissolved by the water. Heat 200 c.c. of absolute alcohol in a round-bottom flask on a water bath until the alcohol boils. Meanwhile, weigh out about 12 grms. of bright, perfectly dry, metallic sodium freed from naphtha by pressing between folds of blotting paper. As soon as the alcohol begins to boil, add sodium, cut into small pieces, one piece at a time, to the alcohol. The reaction is violent; large volumes of hydrogen and alcohol vapour escape. Hence keep the flask covered with a watch-glass or small funnel to avoid loss by spurting. The violence of the reaction gradually diminishes. When the reaction is over, sodium alcoholate, small bits of metallic sodium, and alcohol remain in the flask.

Add the hot water, freed from carbon dioxide, in small quantities at a time to the flask containing the sodium alcoholate, etc. Boil off the alcohol by aspirating air through the flask containing the hot liquid. When the solution no longer smells of alcohol, cool the flask quickly; add cold water freed from carbon dioxide. Transfer the mixture to a litre flask and dilute with CO_2-free water to the mark on the neck. Shake. The solution quickly absorbs carbon dioxide from the air. Hence, let the neck of the flask be plugged with a rubber stopper fitted with a soda-lime tube as shown in fig. 33. The strength of the solution must be determined by titration with standard hydrochloric acid. It is best to work with the solution as it stands, approximately half-normal, to avoid risk of contamination by exposure to the air.

If the temperature of the soda solution be more than 3° different from the standard, an allowance must be made for expansion or contraction. The following correction table (Table XIII.) is used, as has been indicated by example, Tables VIII. and XI. (pages 29 and 49), and when the temperature of the soda solution differs more than 3° from the standard 15°.[3] For solutions more dilute, say $\frac{1}{10}$N, the table for water (page 29) is used.

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[1] E. Fleischer (*Chem. News*, **19.** 303, 1869) prefers a mixture of Glauber's salt and caustic lime. A. Beutell, *Chem. Ztg.*, **12.** 86, 1887.

[2] F. W. Küster, *Zeit. anorg. Chem.*, **13.** 134, 1897; **41.** 474, 1904; W. A. Smith, *Zeit. phys. Chem.*, **25.** 155, 1898; H. Ley, *ib*, **30.** 205, 1899; W. R. Bousfield and T. M. Lowry, *Phil. Trans.*, **204.** 253, 1905; E. Neitzel, *Zeit. anal. Chem.*, **32.** 422, 1893; W. N. Hartley, *Journ. Chem. Soc.*, **26.** 123, 1873; C. P. Hopkins, *Journ. Amer. Chem. Soc.*, **23.** 727, 1901. For explosions during the preparation of standard sodium hydroxide from metallic sodium, see A. Harpf and H. Fleissner, *Zeit. chem. Apparatenkunde*, **1.** 534, 1906; F. W. Küster, *ib.*, **2.** 535, 1906. For the preparation of colourless alcoholic solutions of potassium hydroxide, H. Thiele and R. Marc (*Zeit. öffent. Chem.*, **10.** 386, 1904) recommend the use of potassium sulphate and barium hydroxide. See R. Gaze, *Apoth. Ztg.*, **25.** 668, 1910.

[3] This table may also be used for N-H_2SO_4; N-HNO_3; N-Na_2CO_3; N-NaOH. It is based on A. Schulze, *Zeit. anal. Chem.*, **21.** 167 1882, and it can be easily adapted to other standard temperatures.

Table XIII.—Temperature Corrections for Normal Soda Solutions.
(Standard temperature, 15°.)

Temp.	0	1	2	3	4	5	6	7	8	9
	...	...	...	...	...	+2·0	+1·9	+1·7	+1·5	+1·3
1	+1·1	+0·9	+0·7	+0·5	+0·3	Unit.	−0·2	−0·5	−0·7	−1·0
2	−1·3	−1·5	−1·8	−2·1	−2·4	−2·7	−3·0	−3·4	−3·7	−4·0

§ 30. The Errors of Experiment in Volumetric Analysis.

The principal errors incidental to volumetric work are: (1) unrecognised changes in the strength of the standard solutions; (2) inaccurate measuring instruments (page 28)—with care, these can usually be kept below 0·1 per cent.; (3) weighing the substances used in the analysis (page 27)—the errors in weighing need not exceed 0·1 per cent.; (4) the use of dirty burettes, and drainage errors previously discussed; and (5) a small excess of the standard solution is needed before the indicator will show the end of the reaction—this error is somewhat variable in magnitude, and depends upon a number of factors. For instance, it depends upon the amount and concentration of the standard solution used in the titration, and on the magnitude of the drops falling from the burette. In the regular types of burette, one drop is nearly 0·05 c.c. Hence, if the reaction be not completed on the addition of the last drop, and completed with the addition of one drop more, it is often assumed that half a drop, namely, 0·025 c.c., completed the reaction.[1]

The smaller the amount of substance used in the analysis, the smaller the volume of the standard solution required for the titration, and the greater the error of experiment. If 4 c.c. of the standard solution be used, half a drop, namely, 0·025 c.c., may lead to an error of 0·62 per cent.; whereas, if 40 c.c. of the standard solution be needed for the titration, the corresponding error would be 0·062 per cent.

Again, suppose three independent determinations of the ferric oxide be made on a given clay by titration with permanganate solution (1 c.c. representing 0·002527 grm. Fe_2O_3), and 1·0, 1·01, and 1·1 c.c. were respectively required. The corresponding percentage amounts of ferric oxide would be respectively 0·2527, 0·2552, and 0·2780 grm. Suppose, further, that with another sample of clay 10·0, 10·01, and 10·1 c.c. of permanganate were needed in three independent titrations. The corresponding percentage amounts of ferric oxide would be 2·527, 2·529, and 2·552 grms. respectively. Again, suppose that 100·0, 100·01, and 100·1 c.c. of permanganate were needed with a third sample of clay. The corresponding amounts of ferric oxide would be 25·270, 25·272, and 25·297 grms. Hence, the greater the volume of the standard solution used in the titration, the less the effect of small deviations in the measurement of the volume of the standard solution on the final result.

Consequently, *it is advisable to arrange the quantity of substance to be analysed, and the strength of the standard solution, so that a comparatively large volume of the standard solution is used.* Since 50-c.c. burettes are generally employed, something rather less than 50 c.c. is a convenient amount. For instance, 5 c.c.

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[1] In some processes, the "excess" of standard solution needed to produce a colour with the indicator is specially determined. This is done, for instance, in the uranium process for phosphorus (page 600); the ferrocyanide process for zinc (page 367); the chromate process for chlorides (page 79); etc.

of concentrated hydrochloric acid (sp. gr. 1·14) will require over 40 c.c. of N-NaOH solution.[1] If an acid of sp. gr. 1·015 be in question, this has 32 grms. of HCl per 1000 c.c. Hence, 5 c.c. of this acid has 0·16 grms. of HCl. This would only take about 4 c.c. of N-NaOH. Hence, it is advisable to use a more dilute soda solution, say $\frac{1}{10}$N-NaOH, in which case, about 40 c.c. of the standard solution will be needed. For the analysis of more dilute solutions of acid, more dilute solutions of alkali will be needed—say $\frac{1}{100}$N-NaOH.[2] It does not follow that the weaker the standard solution the more accurate the titration, because, if the standard solution be too weak, a relatively large volume will be required to colour the indicator after the end of the reaction, and nothing is really gained in accuracy.

The above principles can be discussed from another point of view. Suppose 2N-acid is used for the titration of a gram of sodium hydroxide, then 1 c.c. of the 2N-acid will represent 8 per cent. of NaOH, and 0·1 c.c. will represent 0·8 per cent. of NaOH. Unavoidable variations in the amounts of standard acid required for the titration of duplicates will represent an error of 0·2 to 0·3 per cent. NaOH. This error is too great, and it is considerably reduced by using a standard acid but one-fourth the strength, namely, $\frac{1}{2}$N-acid.

It is not advisable to make, say, $\frac{1}{100}$N-NaOH by diluting 10 c.c. of $\frac{1}{10}$N-NaOH to 100 c.c. unless the solution so obtained is standardised. This arises from the fact that a small error in the measurement of the volume of the concentrated solution is multiplied into a relatively large error by the process of dilution. For a similar reason, if a concentrated solution of, say, sp. gr. 1·14 is under investigation, and it is convenient to work with a dilute standard solution, say, $\frac{1}{10}$N-NaOH, it is not advisable to take, say, 0·5 c.c. of the concentrated acid for the titration. Rather should 20 c.c. of the concentrated acid be made up to a litre, and 25 c.c. of this solution be used for the titration. The 25 c.c. of the diluted acid would represent 0·5 c.c. of the concentrated acid.

The reading is obviously the sharper, the narrower the burette. If the burette be narrow, it must have an inconvenient length if it is to hold enough fluid for a titration. A 50-c.c. burette reading to $\frac{1}{10}$ c.c. will be about 60 cm. long, and the tube will have a bore of approximately 11 or 12 mm. In special cases, as in the colorimetric determination of iron, where a burette reading to $\frac{1}{50}$ c.c. is used, the burette is about 0·5 cm. bore, with a capacity of 10 c.c., and yet is 75 cm. long.

These preliminary remarks may be used as a guide in the succeeding problems. For instance, to determine the amount of calcium carbonate in a sample of whiting, and the amount of calcium carbonate in a given sample of ground flint or ground Cornish stone. In the former case, the sample may have 98 per cent. of calcium carbonate, and in the latter, 2 per cent. Since 50 grms. of calcium carbonate will correspond with 1000 c.c. of N-HCl, 1 grm. of calcium carbonate will correspond with 20 c.c. of N-HCl. Hence, if 50 c.c. of N-HCl be added to the gram of whiting, and the excess of HCl be titrated with N-NaOH, we shall require about 30 c.c. of the standard alkali. Again, 5 grms. of calcium carbonate will correspond with 1000 c.c. of $\frac{1}{10}$N-HCl, and 1 grm. of calcium carbonate will correspond with 200 c.c. of $\frac{1}{10}$N-HCl. Hence, if the ground flint contains 2 per cent. of calcium carbonate, 50 grms. of flint will want 200 c.c. of $\frac{1}{10}$N-hydrochloric acid, or 5 grms. will want 20 c.c. of $\frac{1}{10}$N-HCl. Hence, if 50 c.c. of $\frac{1}{10}$N-HCl be mixed with 5 grms. of flint, the titration of the excess of acid will require about 30 c.c. of $\frac{1}{10}$N-HCl.

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[1] From Table LXXVI., page 679, 100 c.c. of acid, sp. gr. 1·14, has 315 grms. HCl. Hence, since 1000 c.c. of N-HCl has 36·5 grms. of HCl, this is equivalent to 1000 c.c. of N-NaOH. Hence, 40 c.c. of NaOH will be equivalent to 1·46 grms. of HCl. But 315 grms. HCl are in 1000 c.c. of the acid in question; hence, 1·46 grms. HCl will be found in approximately 5 c.c. of the given acid.

[2] To avoid frequently refilling the burette when many titrations have to be made, see the "automatic burettes," page 55.

§ 31. Direct Titrations—Sodium and Potassium Carbonates.

Suppose that it be required to determine the amount of sodium carbonate in a given sample of soda ash. A quantity of the powdered soda ash is placed in a weighing bottle, and dried at 100°. When cold, the bottle and contents are weighed. A portion, approximately 1 grm., is transferred to an Erlenmeyer's flask, say 400 c.c. The weighing bottle and contents are again weighed. The difference between the two weights gives the amount of soda ash transferred to the flask:

Weighing bottle and powder (before)	25·2931 grms.
Weighing bottle and powder (after)	24·1110 grms.
Amount of soda ash	1·1821 grms.

Add about 150 c.c. of water. When all is dissolved, add about two drops of a solution of methyl orange, and titrate the solution with $\frac{1}{2}$N-HCl as indicated on page 65. Suppose that the mean of three experiments shows that 43·6 c.c. of the standard solution have been used. Then, since

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2,$$

26·5 grms. of sodium carbonate correspond with 18·235 grms. of hydrogen chloride; and since 1000 c.c. of the half-normal acid are equivalent to 26·5 grms. of sodium carbonate; or, 1 c.c. of acid represents 0·0265 grm. of Na_2CO_3; or, 43·6 c.c. of the semi-normal acid represent $0·0265 \times 43·6 = 1·1554$ grms. Na_2CO_3 per 1·1821 grms. of sample; hence, 100 grms. of the sample have 97·74 grms. of Na_2CO_3, *i.e.* 97·74 per cent. of sodium carbonate.

All this arithmetic is summarised in the expression:

$$\frac{2·65n}{w} = \text{per cent. of } Na_2CO_3,$$

where n represents the number of cubic centimetres of the standard $\frac{1}{2}$N-HCl used in the titration, and w is the weight of powder used for the titration.

It will be obvious that if w be exactly 2·65 grms., the number of c.c. used in the titration will represent directly the percentage amount of Na_2CO_3 in the given sample.[1] It is sometimes most convenient to work according to the latter system (page 54). This question has to be solved: Is it quicker to weigh exactly the required amount, say, 1·325 grms., or to take an approximate weight and calculate the corresponding amount of sodium carbonate as indicated above? The answer will largely depend upon the number of determinations to be made, and whether the weight of the powder is likely to change by the absorption of moisture, etc., while being weighed.

Washing-soda and pear-lash may be treated by a similar method to that described above.[2]

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[1] In that case we should have to use a 100-c.c. burette, or a normal solution. If 1·325 grms. of powder be weighed, twice n will represent the percentage amount of Na_2CO_3 in the sample.

[2] See page 72 *seq.* for a more detailed analysis of soda ash.

§ 32. Back Titrations[1]—Calcium Carbonate.

Suppose that whiting is to be investigated, weigh about 1 grm. of the dried sample in a weighing bottle, or on a piece of glazed paper.[2] Brush[3] every trace of powder from the paper into a dry 400-c.c. flask. Add, say, 50 c.c. of N-HCl. Take care that no powder sticks to the neck of the flask, and so escapes the action of the acid.[4] When all action has subsided, shake the flask vigorously. Add two drops of methyl orange,[5] and titrate the solution with N-NaOH until the yellow colour of the methyl orange appears.[6] The following results were obtained in an experiment on whiting:—

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[1] F. Mohr, *Liebig's Ann.*, **86**. 129, 1853.

[2] Cut into the form of an elongated ▽. The narrow end is not too wide to pass into the neck of the flask. The paper is folded lengthwise so as to form a kind of gutter. The powder is placed near the broad end, and the narrow end of the paper is placed in the neck of the flask. The flask is then placed upright, and the powder is transferred to the flask by tapping and brushing.

[3] Good camel-hair brushes, with the hair cut rather shorter than the brushes used by painters, are convenient for this purpose. A selected tail-feather of the *Gallus domesticus* (barnyard fowl), trimmed as indicated in fig. 34, is usually more effective than the brush. The brushes and feathers are best kept in the glass box mentioned on page 8.

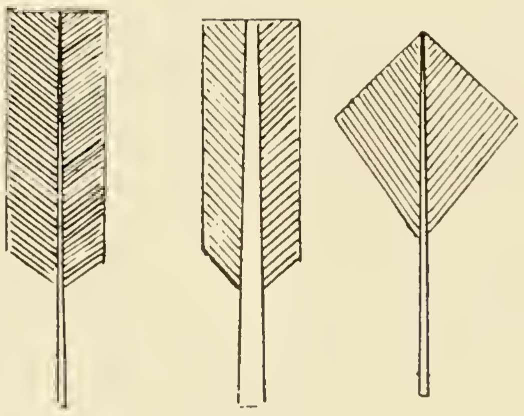

Fig. 34.—Dust brushes.

[4] Erlenmeyer's flasks (fig. 35*a*) with a broad neck are recommended for titrations. The neck and bottom should be such as to permit easy cleaning with the "bottle brush" and "policeman," page 92. When liquids are effervescing or boiling, the neck should be stopped with a bulb made for the purpose, or a funnel. The stoppers are afterwards washed. With the idea of preventing loss by spurting, Bolton's flasks (A. Dettloff, *Chem. Ztg.*, 31. 181, 1907; *German Pat. D.R.P. No.* 183222, 1907; A. Gawalovski, *Zeit. anal. Chem.*, 14. 170, 1875) may be used. These are unsymmetrical Erlenmeyer's flasks (fig. 35*b*). Bolton's flasks are also convenient for decanting a liquid from a solid. The solid is allowed to settle while the flask is resting on a suitable stand (fig. 35*c*). The form shown in fig. 35*d* is due to E. Herzka (*German Pat. D.R.G.M. No.* 435753, 1910). This is an improvement on Bolton's flask for preventing loss by spurting, because the fluid particles are projected against the walls of the flask when a liquid is boiling or effervescing, or when a gas is being passed rapidly through the contents of the flask (fig. 35*e*).

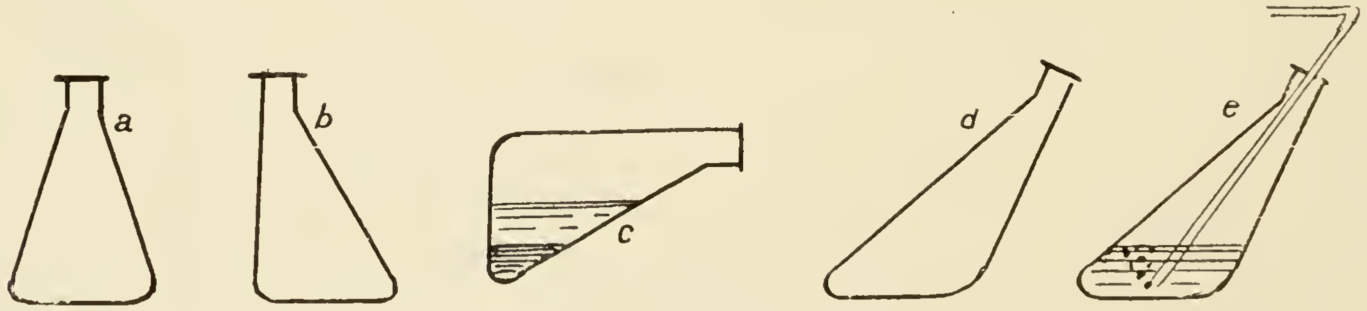

Fig. 35.—Modified flasks.

[5] If phenolphthalein be used as indicator, the solution must be boiled, before the titration, in order to get rid of the carbon dioxide in the solution.

[6] The "transition tint" is often taken as the end point.

Glazed paper and powder	1·9573 grms.
Glazed paper after removal of powder	0·5363 grms.
Whiting	1·4210 grms.

50 c.c. of N-HCl containing 35·2 grms. of HCl per 1000 c.c. were added as indicated above. The acid remaining after the reaction required 25·5 c.c. of N-NaOH containing 39·1 grms. of NaOH per 1000 c.c. From the equation

$$NaOH + HCl \rightarrow NaCl + H_2O$$

it follows that 40·01 grms. of NaOH represent 36·47 grms. of HCl. Hence, 0·0391 grm. of NaOH represents 0·03564 grm. HCl; and 1 c.c. of the NaOH solution represents 0·03564 grm. HCl, or 1·01 c.c. of the acid used for decomposing the whiting. Consequently, 25·5 c.c. of alkali used in the titration represent 25·75 c.c. of the same hydrochloric acid. Hence, 50 – 25·75 = 24·25 c.c. of the same hydrochloric acid were taken up by the whiting. From the equation

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

it follows that 72·94 grms. of HCl represent 100·09 grm. of $CaCO_3$. Hence, 1 c.c. of the given acid (or 0·0352 grm.) represents 0·0483 grm. $CaCO_3$. Hence, the 24·25 c.c. of hydrochloric acid which reacted with the whiting represent 24·25 × 0·0483 = 1·17 grms. of $CaCO_3$ in the given sample, that is, 82·4 per cent.

If solutions of exact normality had been employed, and 50 c.c. of N-HCl and 25·7 c.c. of N-NaOH were required, it follows that 50 – 25·7 = 24·3 c.c. of N-HCl would be taken up by the whiting. But 1 c.c. of the N-HCl represents 0·050 $CaCO_3$; consequently, 24·3 c.c. of the N-HCl represent 1·215 grms. of $CaCO_3$ in the 1·421 grms. of sample, or the sample has 85·5 per cent. $CaCO_3$.

Summarising this arithmetic, if n represents the number of cubic centimetres of N-NaOH used in the titration, $50 - n$ represents the number of cubic centimetres of N-HCl "consumed" by the whiting. Hence, if w represents the weight of the sample in grams, the sample has

$$\frac{5(50 - n)}{w} = \text{per cent. of } CaCO_3.$$

If we make $w = 1·6667$ grms., and use normal solutions of acid and alkali, it follows that $3(50 - n)$ will give the percentage amount of $CaCO_3$ in the sample.

A similar method can be used for evaluating $BaCO_3$, ZnO, $MgCO_3$, MgO, etc. The method can be employed for determinations of the amount of calcium carbonate in samples of ground flint, ground stone, etc. A given weight of these materials is treated with deci-normal acid and alkali as indicated above. For instance, 5 grms. of flint (dried at 110°) were digested with 50 c.c. of $\frac{1}{10}$N-HCl on a water bath. The cold solution was titrated with $\frac{1}{10}$N-NaOH. The mean of three experiments gave 39·51 c.c. of $\frac{1}{10}$N-NaOH. Hence, 50 – 39·51 = 10·49 c.c. of $\frac{1}{10}$N-HCl were taken up by the calcium carbonate in the flint. But 1000 c.c. of $\frac{1}{10}$N-HCl correspond with 5·0 grms. of $CaCO_3$; hence, 10·49 c.c. correspond with 10·49 × 0·005 = 0·05245 grm. of $CaCO_3$ per 5 grms. of flint—that is, 1·05 per cent. $CaCO_3$. Summarising the arithmetic, it follows that $\frac{1}{10}(50 - n)$ here represents the percentage amount of $CaCO_3$ in the given sample.

It will be observed that if $\frac{1}{100}$N-NaOH had been used for the back titration with the idea of obtaining more exact results, it will be obvious that *the increased accuracy is illusory*, for the accuracy of the process depends on the exactness of the measurement of the more concentrated solution.

§ 33. Back Titration—Mixed Hydroxides and Carbonates.

Suppose it be required to determine the amount of caustic soda in a given sample of soda ash.[1] Dissolve, say, 50 grms. in warm water, filter and wash the insoluble matter, if any be present.[2] Make the washings up to 1 litre. Titrate 20 c.c., equivalent to 1 grm., as indicated above with $\frac{1}{2}$N-acid and methyl orange as indicator. This titration includes sodium carbonate as well as caustic soda and sodium sulphide, if these be present. To determine the caustic soda, pipette, say, 40 c.c. into a 200-c.c. flask, add a slight excess[3] of barium chloride (20 c.c. of a 10 per cent. solution will suffice). Barium carbonate is precipitated. Make the liquid with the solid in suspension up to the mark with cold distilled water. Shake the corked flask. When the solution is cold,[4] make it up to the mark on the neck with cold distilled water. Shake the flask. Either let the precipitate settle, and pipette off 50 c.c. from the clear, or filter a portion of the solution, and take 50 c.c. from the clear filtrate.[5] The standard flask shown in fig. 36 will be found very convenient for withdrawing aliquot portions from, say, a litre of solution. It is an ordinary litre flask with a side tap sealed on to the flask before graduation, as shown in the diagram. Titrate the 50 c.c. with, say, $\frac{1}{10}$N-HCl, using methyl orange as indicator. Each cubic centimetre of the solution will represent 0·004006 grm. of NaOH per gram of soda ash.[6]

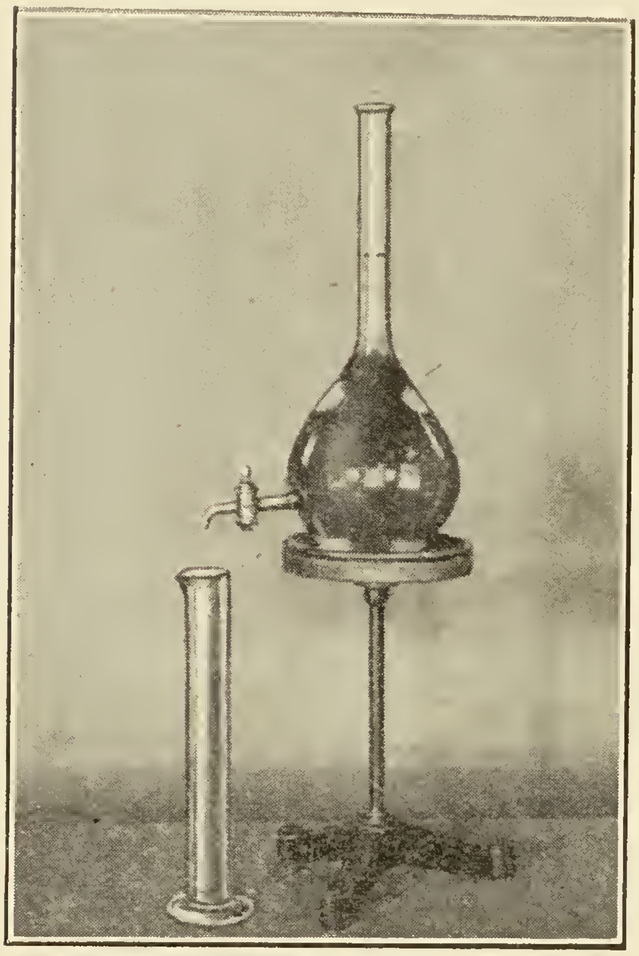

FIG. 36.—Measuring liquids.

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[1] For another method, see page 64. The method in the text is due to C. Winkler. A. C. Andersen, *Tidskr. Kem. Farm. Terapi*, 11. 161, 1908 ; *Journ. Pharm. Chim.*, 28. 370, 1908 ; R. B. Warder, *Chem. News*, 43. 228, 1881 ; G. Lunge and W. Lohhöfer, *Zeit. angew. Chem.*, 14. 1125, 1901 ; G. Lunge, *ib.*, 10. 169, 1897 ; J. Tillmans and O. Heublein, *ib.*, 24. 874, 1911. (There is an error due to the escape of carbon dioxide obviated by the method indicated in the text.) F. W. Küster, *Zeit. anorg. Chem.*, 13. 142, 1897 ; C. F. Cross and E. J. Bevan, *Zeit. anal. Chem.*, 37. 685, 1898 ; K. Novolny, *Zeit. Electrochem.*, 11. 453, 1905 ; M. le Blanc and K. Novolny, *Zeit. anorg. Chem.*, 51. 181, 1909 ; M. le Blanc, *ib.*, 53. 344, 1907 ; F. W. Küster, *ib.*, 13. 127, 1896 ; S. P. L. Sörensen and A. C. Andersen, *Zeit. anal. Chem.*, 47. 279, 1908 ; H. Seger and E. Cramer, *Tonind. Ztg.*, 18. 593, 1894.

[2] The amount can be estimated by drying and weighing, if needed (page 155).

[3] According to W. Smith (*Journ. Soc. Chem. Ind.*, 1. 85, 1882), if a large excess of barium chloride be used, some alkali will be lost by absorption. Exact precipitation is necessary to secure accuracy. S. P. L. Sörensen, *Zeit. anal. Chem.*, 45. 220, 1906 ; 47. 279, 1908.

[4] A COOLING BOX, in cases like this, where speed is essential, will be found a great convenience. This can be made of wood lined with sheet lead or sheet copper, and provided with entrance and overflow pipes for the cold water. The flask or flasks to be cooled are placed in the box, and a current of water allowed to flow through the box. To prevent the flasks overturning, either a series of lead rings can be provided to fit on the necks of the flasks, or a shelf with sockets may be fitted to the box.

[5] According to A. Müller (*Journ. prakt. Chem.* (1), 83. 384, 1861) the filter paper absorbs an appreciable quantity of the barium salt, and gives low results. But here we are now only concerned with the sodium hydroxide.

[6] Sodium sulphide, if present, will be included in this result, and a deduction must be made after the sulphides have been determined.

Sulphides in the presence of chlorides can be determined volumetrically by Lestelle's process,[1] in which 100 c.c. of a solution containing the equivalent of, say, 5 grms. of soda ash are titrated with an ammoniacal solution of silver nitrate,[2] until no black precipitate of silver sulphide—Ag_2S—is formed on adding another drop of the silver nitrate solution. To observe the end of the titration accurately, the solution is filtered towards the end of the operation,[3] and the titration is continued if necessary. It may be necessary to repeat the filtration a number of times. With the above proportions, 1 c.c. of the standard solution represents 0·1 per cent. of sodium sulphide in the given sample.[4]

Sulphites are determined by acidulating 100 c.c. of a solution containing the equivalent of 5 grms. of the sample with acetic acid. Add starch solution, and titrate with a standard iodine solution[5] until the blue colour of starch iodide permanently appears. For every 1 c.c. of the silver solution used in the sulphide test, deduct 1·3 c.c. from the iodine solution used in the titration. Each c.c. then represents 0·000001613 grm. Na_2SO_3, or 0·0000323 per cent. of Na_2SO_3.

Sodium sulphate is best determined gravimetrically as barium sulphate (page 618); sodium chloride is determined by Mohr's process (page 79); iron, by the permanganate process (page 198); and sodium silicate, by evaporation with hydrochloric acid (page 167).

§ 34. Correction for the Volume of Suspended Solids.

It is here necessary to examine the nature of the error due to the assumption that the solid barium carbonate in suspension occupies no appreciable volume. The error will obviously be negligibly small when the volume of the solid is small in comparison with the volume of the solution, but the error may be appreciable when the volume of the precipitate is large in comparison with the volume of the flask.[6] It is therefore necessary to look into this subject more closely.

By a previous titration we found the amount of "sodium carbonate" per 20 c.c. of solution. Let a represent the "sodium carbonate" in the 100-c.c. flask. One gram of sodium carbonate is equivalent to 1·862 grms. of barium

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[1] H. Lestelle, *Compt. Rend.*, **55**. 739, 1862.

[2] Ammoniacal Silver Nitrate.—Dissolve 13·810 grms. of silver in pure nitric acid, add 250 c.c. of concentrated ammonia, and dilute the solution to a litre. 1 c.c. represents 0·005 grm. Na_2S. The ammonia keeps the silver chloride in solution.

[3] Some recommend a Beale's tube for this purpose. A piece of filter paper is tied over the lower end *A*, fig. 37, and a piece of muslin is tied over the paper to prevent it breaking. When

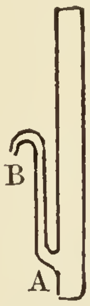

Fig. 37.—Beale's filter pipette.

the end *A* is dipped in the mixture, clear liquid rises in the cylinder. This is poured from the little spout *B* and tested. If the titration be not completed, the liquid withdrawn must be returned to the main solution.

[4] If no sulphites are present, the titration for sulphides is best made by the process used for sulphites.

[5] Iodine solution: 3·249 grms. of iodine per litre. See page 288 for details—preparation, precautions, etc.

[6] O. Eberhard, *Zeit. öffent. Chem.*, **4**. 867, 1898; M. Ruoss, *Zeit. anal. Chem.*, **37**. 422, 1898; M. Bicard and H. Pellet, *Zeit. anal. Chem.*, **24**. 460, 1885; *Bull. l'Assoc. Chim. Sue.*, **1**. 230, 1885; E. Lenoble, *Bull. Soc. Chim.* (3), **11**. 336, 1895; W. R. Smith, *Journ. Amer. Chim. Soc.*, **31**. 935, 1909. Advantage may be taken of the fact that dilute solutions of oxalic acid exert no appreciable action on alkaline earthy carbonates, to titrate with standard oxalic acid all the liquid with the precipitate instead of an aliquot portion. Phenolphthalein as indicator.

carbonate. Hence, *a* grms. of sodium carbonate, found by titration, will be equivalent to 1·862*a* grms. of barium carbonate. The specific gravity of dry barium carbonate is 4·3. Hence, the volume of the barium carbonate will be 0·433*a* c.c. If the soda ash contained 98 per cent. of sodium carbonate, $a = 0·98$. Hence, the barium carbonate in the 100-c.c. flask occupied $0·98 \times 0·433 = 0·424$ c.c. Hence, the 100-c.c. flask contained $100 - 0·424$, or 99·6 c.c. By drawing off 50 c.c. for the titration we drew, not the equivalent of 0·5 grm., but of 0·504 grm. Hence, each c.c. of the $\frac{1}{10}$N-acid represents 0·004006 grm. of NaOH per 1·04 grms. of the soda ash, or 0·003974 grms. NaOH per grm. of soda ash. The error may be somewhat serious when appreciable amounts of NaOH are in question, although the correction is usually neglected in practice.[1]

The process just indicated may be a little more complicated. In determining soluble sulphates, a known amount of barium chloride may be added to the slightly acidified solution. The solution is boiled to get rid of carbon dioxide and then exactly neutralised. An excess of standard solution of sodium carbonate is then added. The solution is made up to a definite volume and the excess of sodium carbonate in an aliquot portion of the clear titrated with standard acid. This gives data sufficient to calculate the amount of barium chloride which reacted with the sodium carbonate. The remaining barium chloride must have reacted with the soluble sulphates. We have both barium sulphate and barium carbonate in suspension. For the sake of illustration, assume that it is required to calculate the amount of barium chloride in a given solution. Add an excess of sodium carbonate, say, N or 1000 mgrms. (*i.e.* 1 grm.), and make the solution with the precipitate in suspension up to the V c.c. mark in a standard flask, say, $V = 50$ c.c. Either pipette or filter v c.c. of the clear solution, suppose $v = 25$ c.c. The sodium carbonate is determined by titration with standard acid. Suppose that 22·35 c.c. of $\frac{1}{5}$N-acid are needed. Hence, 50 c.c. needed $22·35 \times 2 = 44·7$ c.c. of $\frac{1}{5}$N-acid; then the excess of sodium carbonate, w, was $44·7 \times \frac{1}{5} \times 53 = 473·8$ mgrms. But 1 grm. of sodium carbonate is equivalent to 1·862 grms. barium carbonate; and $1000 - 473·8 = 526·2$ grms. of sodium carbonate will represent $a = 1·862 \times 526·2 = 979·8$ mgrms. barium carbonate, or

$$a = 1·862(1000 - w) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This number $a = 979·8$ mgrms. is not quite right, because we did not allow for the volume of the precipitate in drawing off the 25 c.c. of clear solution. Let A be the right value which would have been obtained had the precipitate been filtered off, washed, and the filtrate made up to the 100 c.c. Then,

$$A = 1·862(1000 - W) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where W represents the correct excess of sodium carbonate which would have been obtained in the filtrate if the precipitate occupied a negligibly small volume. Let s denote the specific gravity of the precipitate (sp. gr. $BaCO_3 = 4·3$). The precipitate then occupies $A/1000s$ c.c., and

$$W = w - \frac{wA}{1000sV}; \qquad w - W = \frac{wA}{1000sV}.$$

The error is then, from (1) and (2),

$$A - a = 1·862(w - W) = \frac{1·862aw}{1000sV}.$$

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[1] Say, checking the composition of black ash; *vide* Lunge (*l.c.*). The neglect may be sometimes justified when comparable results are alone required. In some cases the error might even be greater than the percentage amount of the constituent in question. A different method of analysis, of course, is then used.

Consequently,

$$A - a = \frac{1{\cdot}862AW}{1000sV - A} = \frac{1{\cdot}862aw}{1000sV - 1{\cdot}862w}.$$

The terms A and $1{\cdot}862w$ in the denominators are very small in comparison with $1000sV$, so that these terms can be omitted without materially affecting the value of the fractions. Hence, the error

$$W - w = \frac{1{\cdot}862 \times 473{\cdot}8 \times 979{\cdot}8}{1000 \times 4{\cdot}3 \times 50} = 4{\cdot}0 \text{ mgrms.}$$

Hence the total weight of the barium carbonate is $979{\cdot}8 + 4{\cdot}0 = 983{\cdot}8$ mgrms. The amount of barium chloride corresponding with this barium carbonate is readily calculated. All this arithmetic may be summarised in the formula:

$$\text{Weight of precipitate} = r(N - w)\left(1 + \frac{w}{1000sV}\right) \quad . \quad . \quad . \quad (3)$$

where N denotes the weight of the precipitating agent in mgrms. (1000); s, the specific gravity of the precipitate (4·3); V, the volume of the measuring flask (50); w, the excess of the precipitating agent (473·8); and r, the ratio of the equivalent weight of the precipitate and precipitating agent ($98{\cdot}685 \div 53{\cdot}00 = 1{\cdot}862$). A great many "rapid" processes involve the use of one or other of these two methods of correction. Once the reasoning is understood, there is no need to go through all the steps. The numbers corresponding with the letters can be substituted directly in formula (3).[1]

A mathematical formula is not the end, but the means of attaining the end. Students sometimes get the opposite idea, just as if a builder erected a mansion for the sake of showing off the ladders and scaffolding employed in its construction.

§ 35. Sodium Silicate—Water-Glass.

In commercial water-glass—sodium silicate—the ratio $SiO_2 : Na_2O$ generally lies between 2 : 1 and 4 : 1. In analysis, it is generally assumed[2] that free caustic alkali is present when this ratio falls below 1 : 1, corresponding with about 50·8 per cent. of Na_2O, or with $Na_2O.SiO_2$. Water-glass is found on the market in the form of a solid yellowish or greenish glass, or in a more or less viscid aqueous solution.

For analysis, 10 grms. of the solid are ground to a very fine powder and dissolved in hot water, or 20 grms. of the liquid are digested in water. In both cases the solution is made up to 500 c.c. The solution is allowed to stand some time in order to allow the insoluble matters to settle as a sediment,[3] and to allow air-bubbles to rise to the surface.

1. *Combined and Free Alkali.*[4]—Titrate 100 c.c. of the clear solution with N- or $\frac{1}{2}$N-HCl, using phenolphthalein as indicator. The action of the acid is represented by the equation

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3.$$

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[1] It is also possible to compute the volume of the solid matter in suspension by an application of the principle indicated in § 33, page 72.

[2] There are some reasons for doubting if the assumption is valid.

[3] The sediment can be filtered off, washed, and determined later. J. Ordway, *Chem. News*, 9. 61, 1864.

[4] The term "combined alkali" does not here include the alkali which may be present in the form of neutral salts—sodium chloride, etc. There is usually so little sediment that the correction indicated on page 73 is not needed.

The liberated silicic acid does not affect the indicator. The reaction towards the end is very slow, and the indicator may appear to be permanently decolorised before the reaction is complete. There is therefore some danger of under-titration. If, however, a large excess of sodium chloride be added before the titration, this difficulty does not give much trouble.[1] From the preceding equation, we see that every c.c. of N-hydrochloric acid corresponds with 0·031 grm. of Na_2O. Hence, if w grms. of the sample were made up to 500 c.c., and 100 c.c. taken for the titration, and if n c.c. of the N-hydrochloric acid were consumed in the titration, the sample has $0{\cdot}155n$ grm. of Na_2O per w grms. of sample.

2. *Free Alkali.*—To 100 c.c. of the solution,[2] add 100 c.c. of a solution of 10 grms. crystalline barium chloride gradually with constant stirring. Make the solution up to 250 c.c. Shake well. Filter through dry filter paper. Reject the first 20–30 c.c., and titrate the next 100 c.c. which passes through the paper with $\frac{1}{10}$N-hydrochloric acid and phenolphthalein.[3] Since 1 c.c. of $\frac{1}{10}$N-hydrochloric acid corresponds with 0·0031 grm. Na_2O, if n c.c. of this acid are used in the titration, $n \times 0{\cdot}0031$ grm. of Na_2O is present in 100 c.c. Hence, $n \times 0{\cdot}0031 \times 2{\cdot}5 = 0{\cdot}00775n$ grm. of Na_2O is present in the 250 c.c. Hence, the sample has $0{\cdot}03875n$ grm. Na_2O per w grms. of the sample taken.

The difference between the results of this and the preceding titration represents the amount of combined alkali.[4]

Calculation.—Suppose that 20 grms. of the powder were made up to 500 c.c., and that 42·4 c.c. of N-hydrochloric acid were required for the first titration, and 3·7 c.c. of $\frac{1}{10}$N-hydrochloric acid for the second titration. The results are expressed :—

Free alkali	0·72	per cent.
Combined alkali	32·11	,,
Silica	63·81	,,
Alkaline chlorides, etc.	...	
Insoluble matters	...	
Water (loss on ignition, page 157)	...	

The basicity[5] of the sample, that is, the ratio $SiO_2 : Na_2O$, or the molecular proportion of the silica to the free and combined alkalies, regarded as soda, is nearly 2.[6]

§ 36. The Volumetric Determination of Silver and Chlorine—Volhard's Process.

When potassium or ammonium thiocyanate is added to a solution of silver nitrate, a white precipitate of silver thiocyanate is formed :

$$AgNO_3 + KCNS = AgCNS + NH_4NO_3.$$

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[1] R. T. Thomson (see page 63); C. Lunge and W. T. Lohöfer, *Zeit. angew. Chem.*, 14. 1125, 1901.

[2] The solution should be as concentrated as possible. Hence, some prefer to take 10 grms. made up to 100 c.c. for this determination.

[3] P. Heermann, *Chem. Ztg.*, 28. 883, 1904. If sodium carbonate be present, it will be precipitated as barium carbonate by the barium chloride

[4] The term "alkali" used here is supposed to represent soda, but potash may be present. If a distinction is necessary, a special analysis may be needed to determine the ratio $K_2O : Na_2O$. The silica is determined by evaporating 100 c.c. with hydrochloric acid, as indicated on page 167. The filtrate is treated with ammonia, ammonium carbonate, and ammonium oxalate. Filter. The filtrate is evaporated with hydrochloric acid, ignited to drive off ammonium salts, and the residue is supposed to represent the "alkalies." See page 226 for details. The "total alkalies" so obtained, less the free and combined alkalies, are regarded as alkali belonging to the neutral salts—alkaline chloride, etc.

[5] The term "acidity" might perhaps be more appropriately applied for the ratio $SiO_2 . Na_2O$.

[6] $\text{Basicity} = (63{\cdot}81 \div 60)/(32{\cdot}83 \div 62) = 1{\cdot}96.$

The precipitate is insoluble in nitric acid. The reaction occurs even in presence of ferric salts, and only when all the silver has been precipitated does the thiocyanate react with the ferric salt, forming the characteristic blood-red colour of ferric thiocyanate. The persistent appearance of this coloration shows that the titration is finished. Ferric nitrate or sulphate can be used as indicator, but not the chloride. Similarly, the water and other reagents must be free from chlorides.[1] This method is due to Charpentier, but usually called Volhard's process.[2]

Standardisation of the Solutions.—A standard solution of, say $\frac{1}{10}$N, silver nitrate is made by dissolving 16·989 grms. of pure silver nitrate[3] in water, and making the solution up to a litre with distilled water at 15°. A solution of potassium thiocyanate is made by dissolving 10 grms. of the salt in water and making the solution up to a litre.[4] This latter solution is standardised by pipetting, say, 25 c.c. of the silver nitrate solution into a white porcelain dish.[5] Run the potassium thiocyanate solution from the burette until most of the silver is precipitated[6] as white silver thiocyanate, AgCNS, and then add about 5 c.c. of solution of ferric alum[7] to act as indicator. Each drop of the thiocyanate solution produces a white cloud of silver thiocyanate coloured with a reddish halo of ferric thiocyanate. The colour disappears on shaking, provided any silver nitrate remains in the solution. When all the silver has been precipitated as insoluble silver thiocyanate, one drop of the potassium thiocyanate will colour the solution reddish brown. The colour persists after a vigorous shaking. The reddish-brown colour produced when the titration is not quite finished is but slowly removed when the solution is vigorously agitated. Hence, it is necessary to guard against "under-titration."[8]

Suppose that 24·3 c.c. of the thiocyanate be required for the titration, it follows that 24·3 c.c. of the potassium thiocyanate corresponds with 25 c.c. of silver nitrate, which in turn corresponds with 0·4247 grm. of silver. If the potassium thiocyanate is to be exactly $\frac{1}{10}$th normal, the 24·3 c.c. must be diluted to 25 c.c. Hence, proceed as indicated on page 48.

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[1] Chlorides interfere not only by removing silver as insoluble chloride, but they also interfere with the end point, since silver chloride removes part of the red ferric thiocyanate from the solution.

[2] J. Volhard, *Journ. prakt. Chem.* (2), **9**. 217, 1874; *Liebig's Ann.*, **190**. 1, 1878; *Zeit. anal. Chem.*, **13**. 171, 1874; **17**. 482, 1878; J. B. Schober, *ib.*, **17**. 467, 1878; G. Brügelmann, *ib.*, **16**. 1, 1877; F. A. Falk, *Ber.*, **8**. 12, 1875; B. G. Gentil, *Wochenschr. Pharm.*, **30**. 133, 1903; P. Charpentier, *Bull. Soc. Ing. Civ. France*, 325, 1870; E. Drechsel, *Journ. prakt. Chem.* (2), **15**. 191, 1877; C. Mann, *Oester. Zeit. Berg. Hütt.*, **26**. 426, 1878; H. F. von Jüptner, *ib.*, **28**. 33, 51, 1880; O. Lindemann, *Berg. Hütt. Ztg.*, **35**. 333, 1877; F. T. Shutt and H. W. Charlton, *Chem. News*, **94**. 258, 1906; *Trans. Roy. Soc. Canada*, **11**. 67, 1906; A. Dubosc, *Ann. Chim. Anal.*, **9**. 45, 1904; C. Hoitsema, *Zeit. angew. Chem.*, **17**. 647, 1904; V. Rothmund and A. Burgstaller, *Zeit. anorg. Chem.*, **63**. 330, 1909; E. M. Hamilton, *Min. Scientific Press*, **102**. 364, 1911; A. T. Stuart, *Journ. Amer. Chem. Soc.*, **33**. 1344, 1911; A. E. Knorr, *ib.*, **19**. 814, 1897; T. K. Rose, *Journ. Chem. Soc.*, **77**. 232, 1900.

[3] Powdered and dried at 130° for about an hour. The silver nitrate solution may also be prepared by dissolving 10·8 grms. of pure metallic silver in 50 c.c. of dilute nitric acid. Boil off the nitrous fumes, since they interfere with the indicator later on. Dilute the solution to a litre.

[4] It is very difficult to weigh out exactly the required quantity of the potassium thiocyanate, owing to its deliquescent character. Hence, the solution must be standardised. If a solution of definite strength be required, it is best to take rather more salt than is necessary, and, when the strength of the solution has been determined, dilute the solution as indicated on page 48.

[5] Or in an Erlenmeyer's flask or beaker, and then titrate with a white background as described on page 60.

[6] The results are low if the temperature be much higher than 25°. The nitric acid then "bleaches" the ferric thiocyanate. Sufficient nitric acid should be present to remove the colour produced by the indicator before the titration is finished. An excess of nitric acid does no particular harm, but a large excess gives low results, since it retards the formation of the ferric thiocyanate at the end of the titration.

[7] Ferric Alum Solution: Dissolve 10 grms. of ferric alum in 90 c.c. of water.

[8] In case of "over-titration" a known volume of the standard silver nitrate solution can be added to the solution, and the titration continued Due allowance must, of course, be made for the additional silver.

Determination of Silver.—The titration of the nitric acid solution of the sample[1] under investigation is conducted in the same manner as that described for the standardisation of the potassium thiocyanate solution. The method is valuable provided an accuracy of $\frac{1}{10}$th per cent. will suffice. The results are a little low when large quantities of silver are present, owing possibly to (1) the adsorption of some of the silver nitrate by the precipitated silver thiocyanate; and (2) the action of the precipitate on the solution. The process can also be used in the presence of barium, bismuth, antimony, arsenic, lead, iron, manganese, zinc, etc. Mercury interferes with the titration, since it is precipitated by the thiocyanate. Copper, cobalt, and nickel form coloured solutions and thus interfere with the indicator, although it is claimed that 70 per cent. of copper will not spoil the determination.

Determination of Chlorides.—By this method silver can be estimated in the presence of nitric acid, whereas Mohr's chromate process requires a neutral solution. Hence, the thiocyanate process can be used to estimate the haloids —chlorine, bromine, and iodine—in the presence of phosphates and other salts which give precipitates with silver in neutral solutions, but not in acid solutions. Chlorides, bromides, and iodides in solution are determined by adding an excess of a standard solution of silver nitrate. The excess of silver which has not reacted to form silver chloride is determined by titration with the standard thiocyanate.[2] Thus, W. Dittmar determined chlorides in sea-water by precipitating the chloride with an excess of standard silver nitrate, filtering off the silver chloride, and titrating the excess of silver nitrate as indicated above.

It is important to filter off[3] the precipitate of silver chloride,[4] owing to the fact that the silver chloride reacts with the soluble thiocyanate in such a way that 165 times as much excess $\frac{1}{10}$N-ammonium thiocyanate per 200 c.c. is needed to produce the red coloration in the presence of silver chloride as is needed when the chloride is absent.[5] The results in the presence of the precipitated chloride are more variable, and some 2 per cent. low, under conditions where the results in absence of the precipitated chloride are satisfactorily constant; and but 0·15 per cent. high, when the silver chloride has been filtered off. The presence of sulphates interferes with Volhard's process, because appreciable quantities of silver sulphate are precipitated with the chloride and thiocyanate.[6]

EXAMPLE.—An aliquot portion, say, 20 c.c., of the solution of soda ash indicated on page 72, or an aqueous solution of a gram of the dry salt, is treated with an excess of nitric acid. Then add an excess of, say, 25 c.c. of $\frac{1}{10}$N-silver nitrate solution, and titrate with $\frac{1}{10}$N-potassium thiocyanate solution as indicated above. Suppose that 24·2 c.c. of the $\frac{1}{10}$N-potassium thiocyanate solution are needed. This is equivalent to 24·2 c.c. of the silver nitrate solution. Hence, $25 - 24{\cdot}2 = 0{\cdot}8$ c.c. of the silver nitrate solution has formed silver chloride. But 169·89 grms. of silver nitrate represent 58·46 grms. of sodium chloride. Each c.c. of the silver nitrate solution contains 0·016989 grm. of silver nitrate, which is equivalent to 0·005846 grm. of sodium chloride. Hence, $0{\cdot}8 \times 0{\cdot}005846 = 0{\cdot}0046768$ grm. of sodium chloride. Hence, the sample has the equivalent of 0·47 per cent. of sodium chloride.

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[1] For example, a silver coin dissolved in nitric acid.

[2] For iodides, the nitric acid is added after the standard silver solution.

[3] Say, in a filter tube containing glass-wool (page 102).

[4] M. A. Rosanoff and A. E. Hill, *Journ. Amer. Chem. Soc.*, **29**. 269, 1407, 1907; *Chem. News*, **96**. 264, 274, 299, 1907; G. A. Sanger, *Proc. Amer. Acad.*, **26**. 34, 1879; G. Brügelmann, *Zeit. anal. Chem.*, **16**. 1, 1877; E. Dreschel, *ib.*, **16**. 351, 1877; *Journ. prakt. Chem.*, (2), **15**. 191, 1877; O. Knüpfer, *Zeit. phys. Chem.*, **25**. 266, 1898; L. L. de Koninck, *Chem. Ztg.*, **15**. 1558, 1891.

[5] With bromides and iodides, the interference of the precipitated salt is negligibly small.

[6] L. W. Andrews, *Journ. Amer. Chem. Soc.*, **29**. 275, 1907.

§ 37. The Volumetric Determination of Chlorides—Mohr's Chromate Process.

If a solution of silver nitrate be gradually added to a neutral solution of an alkaline chloride containing a little potassium chromate, silver chloride will be precipitated. The reaction is represented by the equation

$$AgNO_3 + KCl = AgCl + KNO_3.$$

When the reaction is complete, any further addition of the silver nitrate reacts with the potassium chromate :

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3.$$

The permanent red tint of the silver chromate so developed indicates that the reaction between the silver nitrate and the silver chloride is at an end. By using a standard solution of silver nitrate, the reaction is quantitative, and was used by Mohr for the volumetric determination of chlorides.[1]

If acids be present, the chromate may form dichromate, which interferes with the recognition of the end point, and, moreover, acids dissolve appreciable quantities of the silver chromate, and the end point is then indistinct. Hence, any acids which may be present should be neutralised by sodium carbonate, or, better, by pure calcium carbonate. If the solution be feebly alkaline, owing to the presence of a slight excess of carbonate, a little silver carbonate will be precipitated with the chromate. Alkaline solutions should accordingly be neutralised with acetic or nitric acid. A slight alkalinity is not so baneful as a slight acidity.

The Titration.—Dissolve a gram of the dried sample under investigation in water and make the solution up to 100 c.c. Pipette 25 c.c. into an Erlenmeyer's flask and add 1 c.c. of potassium chromate solution.[2] Gradually add $\frac{1}{10}$N-silver nitrate solution[3] with constant stirring or agitation. When the chloride is all precipitated a red coloration of silver chromate will appear, which does not disappear on agitation of the solution. The silver nitrate must be added very slowly towards the end of the titration, so as to run no risk of over-titration. The titration is made with the flask over a sheet of white paper, or a white tile.

A certain amount of silver nitrate is needed to colour the indicator. Hence, Mohr recommends adding, drop by drop, $\frac{1}{10}$N-sodium chloride solution until the red colour of the indicator gives way to the yellow colour of the alkaline chromate. Deduct the volume of sodium chloride so employed from the silver nitrate used in the titration. The result represents the amount of silver nitrate corresponding with the chlorides undergoing titration.

If the precipitate of silver chloride is very large, the end point will be somewhat masked. In that case, add a slight excess, 1–2 c.c., of a dilute standard solution of sodium chloride ($\frac{1}{10}$N). Filter and wash the precipitate twice with water, and again titrate the clear solution, making allowance for the extra sodium chloride added.

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[1] F. Mohr, *Liebig's Ann.*, **97**. 335, 1856. Mohr first used potassium arsenate as indicator ; A. Levol (*Bull. Soc. Encour.*, **52**. 220, 1853 ; *Journ. prakt. Chem.* (1), **60**. 384, 1853) used sodium phosphate ; F. Stolba (*Zeit. anal. Chem.*, **13**. 65, 1874), potassium calcium chromate.

[2] POTASSIUM CHROMATE SOLUTION.—Dissolve 1 grm. of the salt in 100 c.c. of water. The chromate must be free from chlorides. To test for chlorides, dissolve the chromate in water, add a little silver nitrate and then some nitric acid. If the red precipitate which forms dissolves completely, forming a clear solution, chlorides are absent.

[3] SILVER NITRATE SOLUTION.—Dissolve 16·869 grms. of pure silver nitrate in a litre of water. 1 c.c. corresponds with 0·003518 grm. of chlorine. If this solution be standardised by dissolving 5·806 grms. of pure sodium chloride in a litre of water, so as to form a $\frac{1}{10}$N-sodium chloride solution, 25 c.c. of the $\frac{1}{10}$N-sodium chloride will require 25·1 c.c., instead of 25 c.c., of the $\frac{1}{10}$N-silver nitrate solution.

Disturbing Agents.—Salts of lead, bismuth, barium, and iron will form insoluble chromates, and should therefore be absent; coloured salts—cobalt, nickel, and copper—obscure the end point and are therefore objectionable. Pellet[1] has shown that arsenates, arsenites, phosphates, and fluorides do not interfere, since silver chromate forms earlier than silver fluoride, phosphate, etc.

The presence of any salt which augments the solubility of the silver chromate gives high results, since more silver nitrate must be added to produce the red chromate than corresponds with the end of the reaction. Hence, also, salts which augment the solubility of silver chromate should be absent—for instance, the nitrates of the alkalies and alkaline earths,[2] and ammonium salts. The solubility of the silver chromate is also augmented by raising the temperature of the solution,[3] and, in consequence, it is best to titrate cold solutions. An excess of potassium chromate diminishes the solubility of the silver chromate, and, in consequence, a larger quantity of the indicator is employed than would normally be the case. If too little potassium chromate be employed, more silver nitrate is needed to produce the red-coloured chromate.[4]

Difficulty with the Indicator.—In spite of these precautions, a measurable excess of silver nitrate solution must be added after the reaction with the chlorides is ended, before the permanent red colour of the silver chromate is developed. This is particularly noticeable when small quantities of chloride are present in large volumes of solution, and Winkler[5] has accordingly drawn up an empirical correction table (Table XIV.) representing the excess of silver nitrate solution (1 c.c. equivalent to 0·001 grm. chlorine) required to develop the colour of the indicator in 100 c.c. of solution, when 1 c.c. of a one per cent. solution of potassium chromate is employed.

Table XIV.—Correction for Indicator in Mohr's Chromate Process for Chlorides.

Silver solution used.	Deduction.	Silver solution used.	Deduction.	Silver solution used.	Deduction.
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
0·2	0·20	0·8	0·39	5·0	0·50
0·3	0·25	0·9	0·40	6·0	0·52
0·4	0·30	1·0	0·41	7·0	0·54
0·5	0·33	2·0	0·44	8·0	0·56
0·6	0·36	3·0	0·46	9·0	0·58
0·7	0·38	4·0	0·48	10·0	0·60

Of course this table only refers to solutions of the concentration stated. Lunge deducts 0·2 c.c. from the amount of $\frac{1}{10}$N-silver nitrate solution used both in titrating a solution of sodium chloride which requires 50 c.c. of the standard solution, and in titrating sodium sulphate which contains a little sodium chloride. Winkler's experiments show that Lunge's correction is probably about right. Fresenius[1] recommends making the solution to be titrated approximately the same volume and strength as the solution used in standardising the silver solution. Hazen[2] recommends correcting the solution used in titrating by deducting $0·003\,V + 0·02$ c.c. from the standard silver solution, when V denotes the volume of the solution which has just been titrated.

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[1] H. Pellet, *Bull. Soc. Chim.* (2), **28**. 68, 1877.

[2] F. C. Carpenter, *Journ. Soc. Chem. Ind.*, **5**. 286, 1886—sodium and calcium nitrates have least effect; ammonium, potassium, and magnesium the greatest effect. G. Biscaro, *Chem. News*, **53**. 67, 1886.

[3] One part of silver chromate is soluble in 16,666 parts of water at 15·5°, according to W. G. Young, *Analyst*, **18**. 124, 1893.

[4] L. L. de Koninck and E. Nihoul, *Rev. Univ. Mines* (3), **16**. 42, 1891; *Zeit. angew. Chem.*, **4**. 295, 1891.

[5] L. W. Winkler, *Zeit. anal. Chem*, **40**. 596, 1901.

If the correction be neglected when, say, a $\frac{1}{10}$N-silver nitrate solution is used, the resulting error is about 0·4 per cent.[3]

Modification for Small Amounts of Chlorides.—When very small amounts of chlorides are in question, more dilute solutions of silver nitrate are employed—say, 4·795 grms. of silver nitrate per litre; 1 c.c. of this solution represents 0·001 grm. of chlorine; or 2·3975 grms. of silver nitrate per litre; 1 c.c. of this solution represents 0·0005 grm. of chlorine. Suppose that the mixed chlorides obtained in the determination of the alkalies in clays be in question. Add 1 c.c. of the potassium chromate solution. Make the solution up to 50 c.c. in an Erlenmeyer's flask. Add 50 c.c. of distilled water to the same amount of potassium chromate solution in a similar flask; this is used for comparing with the contents of the flask which are being titrated, so that a change of colour of the indicator can be quickly detected. The correction for the amount of silver nitrate solution required to colour the indicator can be made in the same flask.[4] The titration is made over a white porcelain tile, or sheet of white paper. Use a burette reading to $\frac{1}{20}$ths or $\frac{1}{50}$ths c.c. Yellow gaslight gives better results than daylight. Some prefer to work in a dark room with a yellow monochromatic light.[5]

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[1] R. Fresenius, *Quantitative Chemical Analysis*, London, I. 356, 1876.

[2] A. Hazen, *Amer. Chem. Journ.*, II. 409, 1889.

[3] One c.c. of the silver solution corresponds with 0·005806 grm. of sodium chloride. Lunge's correction, 0·2 c.c., corresponds with 0·0011612 grm. sodium chloride. If w grms. of the sample be in question, the percentage error will be equivalent to $0·11612/w$ per cent. of sodium chloride. If $w = 0·2903$ grm., the corresponding error will be 0·4 per cent.

[4] Or use Winkler's Table XIV.

[5] A. Dupré (*Analyst*, 5. 123, 1880) watches the progress of the titration through a flat glass cell, 1 centimetre thick, containing a solution of neutral potassium chromate of approximately the same tint as the solution undergoing titration. The latter appears to be a colourless liquid like water when observed through the cell, and the first appearance of red is easily seen through the cell.

CHAPTER IV.

COLORIMETRY AND TURBIDIMETRY.

§ 38. Colorimetric Methods of Analysis—Colorimetry.

COLORIMETRIC methods for the determination of small quantities of a substance have attracted a great deal of attention, particularly in technical analyses.[1] They have been successfully employed for the determination of iron, manganese, chromium, copper, lead, bismuth, titanium, sulphates, chlorides, ammonia, carbon, silica, phosphorus, etc. They usually offer a quick, simple, and elegant means of determining the amount of a given constituent, and they can sometimes be employed in cases where the amount is too small for gravimetric or volumetric methods. Colorimetric processes are frequently, but not always, more rapid than gravimetric methods.

The choice between colorimetric, volumetric, and gravimetric processes is determined by the particular problem in hand, but *gravimetric or volumetric methods should nearly always be employed when large quantities of the given constituent are in question*—provided, of course, that reliable gravimetric or volumetric processes are available. For small quantities some colorimetric processes far surpass gravimetric processes in accuracy, while others are but crude approximations.

In colorimetry it is assumed that *if two solutions of the same colouring agent in the same solvent have the same tint, they will have the same concentration*, when the depths of the two liquids through which the light passes are the same. Hence, if the concentration of one of the solutions be known, the concentration of the other solution must be the same. This assumption may mean that if w_1 and w_2 respectively denote the weights of colouring matter in the two solutions in the two test glasses, and d_1 and d_2 the corresponding thicknesses of the solutions through which the light passes to the eye, then,

$$w_1 : w_2 = d_1 : d_2 \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

Hence, if any three of these magnitudes be known, the fourth can be calculated by simple proportion. The comparison of the colours of the solutions is done in glass cylinders—called test glasses—made from clear, colourless glass. The instrument used for the comparison is called a *colorimeter*, or *tintometer*. There are three types of colorimeter used in this work.

§ 39. Duboscq's Dipping Colorimeter.

In this instrument[2] the thickness of the liquid in each test glass through which the light passes can be varied until each liquid appears to have the same colour tint. The thickness of the liquid in each tube is measured by a vernier and scale, and since the concentration w_2 of one solution is known, the concentration w_1 of the unknown solution follows at once from (1) above, where

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[1] G. and H. Krüss, *Kolorimetrie und quantitative Spectralanalyse*, Hamburg, 1909.

[2] H. Morton, *Chem. News*, **21**. 31, 1870. See also W. G. Smeaton, *Journ. Amer. Chem. Soc.*, **28**. 1433, 1906; O. Schreiner, *ib.*, **27**. 1192, 1905; G. Steiger, *ib.*, **30**. 215, 1908; C. H. Wolff, *Pharm. Ztg.*, **24**. 587, 1879.

$$w_1 = \frac{w_2 d_1}{d_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Fig. 38 represents a photograph of the front of the apparatus. The operator stands on the right. Fig. 39 represents the path of the light inside the instrument. The diffused light of a lamp or of a monochromatic burner is the source of illumination. This light is reflected from the mirror *A*, and two beams pass respectively through the tubes *B*. The beam of the right is reflected twice in the right half of the prism *K*, and passes through lenses *M N* of the eyepiece, where it only illuminates the right half of the field. The beam on the left follows a similar path, and finally illuminates the left side of the field. Hence, the two halves of the field *P* are only illuminated by the beams of light (dotted in the diagram) passing through the two sets of tubes *B* and *D*.[1]

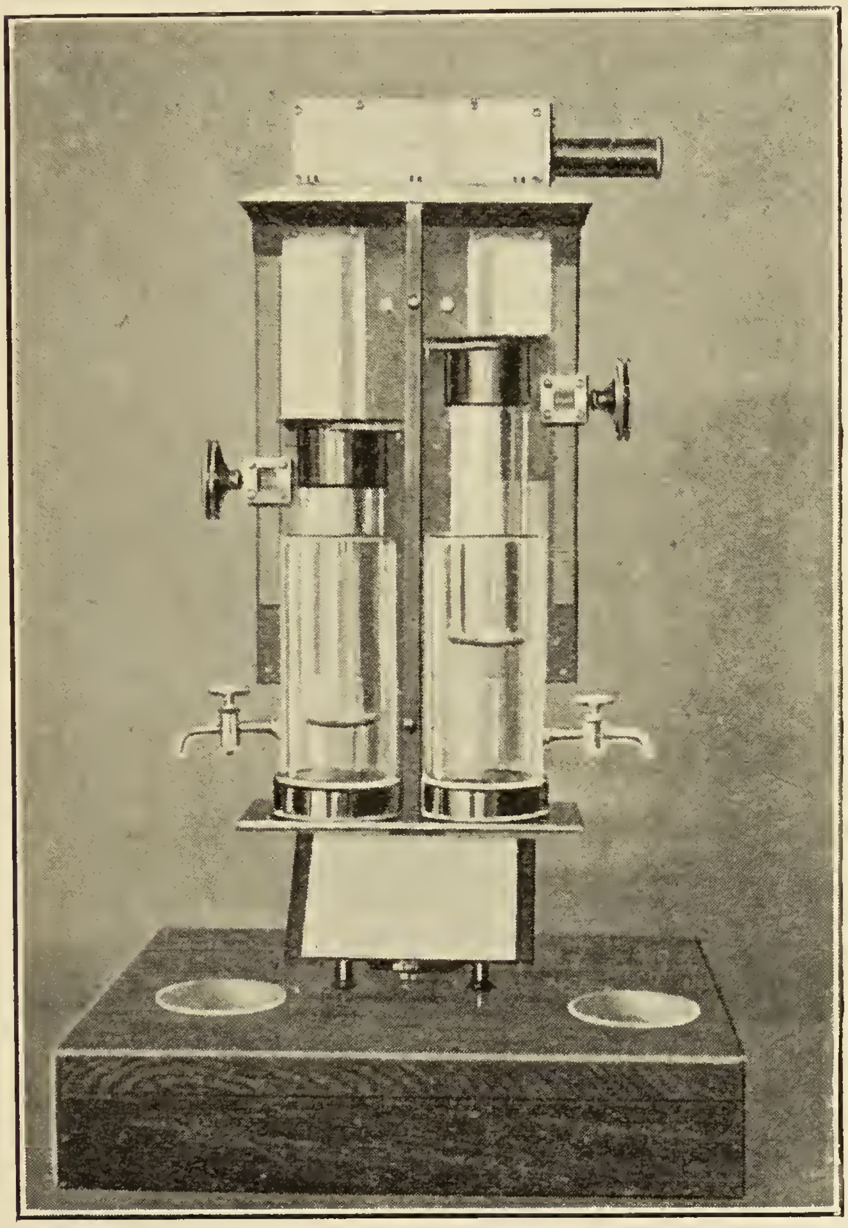

FIG. 38.—Duboscq's colorimeter.

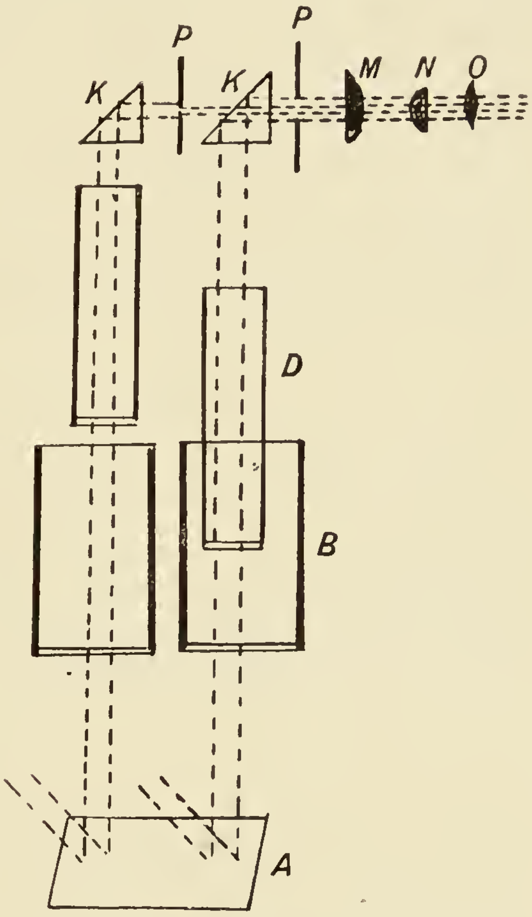

FIG. 39.—Course followed by light in the colorimeter.

To illustrate by example: the solution of unknown concentration was made up to 250 c.c. and placed in the left test glass *A* of Duboscq's colorimeter; the standard solution containing 0·01 grm. of titanic oxide per 100 c.c., that is, 0·025 grm. per 250 c.c. This solution was placed in the right test glass *B*.

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[1] To clean the apparatus, raise the tubes *D*, remove the tubes *B*, and take off the glass at the bottom. The tubes *B* and *D* can then be cleaned. Polish the rest of the apparatus with chamois leather.

The amount of liquid placed in the tubes must not be so great that liquid overflows when the tubes are lowered to the bottom of B. Lower the tubes D until they touch the bottom of the tubes B. The verniers now mark zero, and the two halves of the field in the eyepiece should be uniformly bright (fig. 40*a*); if not, the lamp illuminating the mirror A must be moved until the desired result is attained. Now raise the tube D in the standard liquid until it reaches a point convenient for estimating the tint of the liquid. Then raise D in the other tube until equal tints are obtained in both fields (fig. 40*c*). Read the two scales. Suppose that for $w_2 = 0{\cdot}025$, $d_2 = 2{\cdot}1$ cm.; and $d_1 = 4{\cdot}37$. Hence,

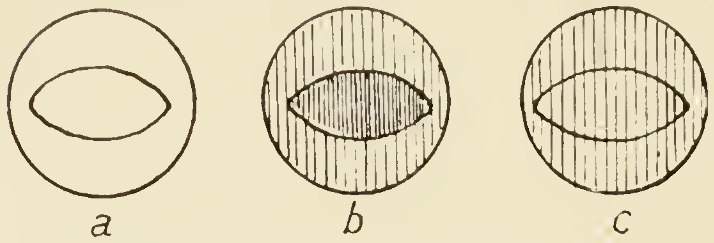

FIG. 40.—Appearance in eyepiece of colorimeter.

$$w_1 = \frac{0{\cdot}025 \times 4{\cdot}37}{2{\cdot}10} = 0{\cdot}052 \text{ grm. per 250 c.c.}$$

Fig. 40*b* represents the appearance of the field of view before the final adjustment (fig. 40*c*).

§ 40. Weller's Colorimeter.

Duboscq's colorimeter and similar instruments are expensive, and are only bought when it is probable that they will save in time what they cost in money. A cheaper instrument, quite efficient for most comparisons, can be made as described below. In this type of colorimeter the two test glasses have the same thickness, the light passes horizontally through each, hence $d_1 = d_2$. Consequently,

$$w_1 = w_2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence, if w_2, in the case of titanic oxide, be 0·052 grm. per 250 c.c. of the standard solution, the same number will also represent the concentration w_1 of the titanic oxide in the unknown solution per 250 c.c., when the tints of the two solutions are the same. Weller's[1] and Hillebrand's colorimeters may be cited in illustration. These are easily made. A wooden box C, about 35 cm. long and 12 cm. square, is stained dead black[2] inside and out. The ends are open. A ground-glass partition is placed at B (fig. 41), and a blackened shutter S slides stiffly up and down 3 to 3·5 cm. behind the glass partition. Two test glasses are selected, of square section, 8 to 12 cm. high, and 3 to 3·5 cm. side. These glasses are placed between the two partitions when in use.[3] Two methods of conducting the determination are indicated on pages 201 and 205.

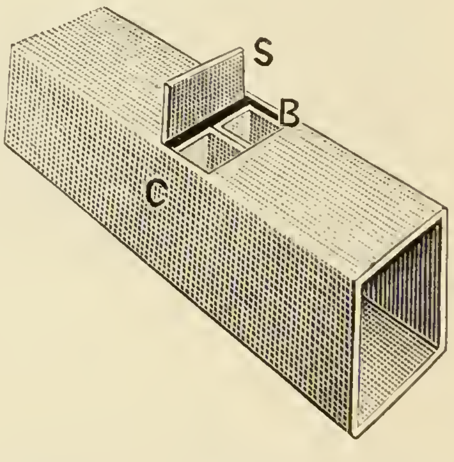

FIG. 41.—Weller's colorimeter (modified).

J. W. Lovibond[4] has devised sets of "standard" coloured glasses; each set has the same colour, but the glasses are regularly graded in depth of tint. By superimposing glasses from the same and different sets—red, blue, yellow—composite colours can be obtained. In this way the tint of a liquid placed in a test glass with parallel sides at a definite distance apart can be matched, and the exact proportion of each component of the colour read off. By finding the tints of a series of standard solutions of known strength once for all, the standard tints so obtained render the subsequent preparation of a standard solution unnecessary provided the same method of preparation is employed. The instrument—"Lovibond's tintometer"—used for the comparison is similar in principle to the instrument indicated in fig. 41, but Lovibond has introduced several improvements which render the results much more accurate—see page 486.

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[1] A. Weller, *Ber.*, 15. 2599, 1882; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 422. 34, 1910; J. W. Mellor, *Trans. Eng. Cer. Soc.*, 8. 123, 1909.

[2] DEAD BLACK PAINT.—Dissolve shellac in methylated spirit; add French polish, and add lampblack. If the mixture dries a dead black which rubs off, more French polish or shellac is needed; if it dries light, more lampblack is needed.

[3] Sold by dealers in chemical apparatus.

[4] J. W. Lovibond, *Journ. Soc. Chem. Ind.*, 7. 424, 1888; *Measurement of Light and Colour Sensations*, London; *An Introduction to the Study of Colour Phenomena*, London, 1905.

§ 41. Nessler's Tubes.

A third method of comparing the tints is commonly used in water analysis. It is rather more tedious than the two methods which precede. The colour is developed in a solution of unknown strength, and in a series of solutions of equal volume but of known strength. The two solutions of known strength which come near to the tint of the test solution are selected, and the colour developed in another series of solutions within narrower limits. This method of trial and failure is repeated until the colour in the test cylinder matches the colour of the standard solution.

The comparison tubes should be selected with great care, and the bottoms should be regular. The bores of the test glasses should be uniform and not tapered. As a matter of fact, the principle of the system is the same as that employed in Weller's colorimeter. Although the cylinders are usually marked "25 c.c.," "50 c.c.," "100 c.c.," it is really the *lengths* of the columns, not the volumes of the solutions, which are compared. Hence, as in Weller's colorimeter, $w_1 = w_2$. It is obvious that in properly matched tubes the volume marks and the heights of the liquids should coincide.

§ 42. Turbidity Methods of Analysis—Turbidimetry.

Turbidity methods resemble colorimetric methods, but instead of comparing the different intensities of the colours of two solutions, the degrees of opalescence of two solutions are compared. The opalescence is produced by the fine-grained solid matter in suspension, which settles very very slowly, and which is not usually removed by filtration in the ordinary manner. For example, traces of silver chloride, barium sulphate, and calcium oxalate.

The action of light on a turbid solution is twofold. (1) The light is dispersed. This gives the solution its characteristic colour. (2) The light is absorbed, so that an object viewed through the liquid appears with diminished distinctness. This latter is the quality compared. It is well to prevent dispersion in the comparison of opalescent solutions as much as possible, by covering the cylinder with, say, a black cloth, and admitting the light from a circular aperture at the bottom. The subject is discussed in more detail, pages 631 and 653.

§ 43. Some Errors in Colorimetry and Turbidimetry.

The most important errors in colorimetry arise from :

(1) *Imperfect perception of the colour.* Colour is a subjective phenomenon due to the action of light on the retina of the eye itself. Possibly no two individuals see exactly the same colour tints in the same substance. A person may be afflicted with a form of colour-blindness and be sensitive to one colour but not to another. Hence, the operator should test himself for any given colorimetric process by matching a standard colour of different intensities against

itself. If concordant results cannot be obtained, the operator must abandon that particular process.

It is here assumed that the operator is normally sensitive to colour impressions. If a person of normal colour sensitiveness examines a coloured liquid with, say, the right eye over the cylinder, and then turns the head suddenly so that the left eye is over the cylinder, the colour *seems* less intense; in another moment, the right eye may be brought over the cylinder—again the colour seems less intense. This shows that first impressions are the stronger, and that the impression imperceptibly weakens in intensity as the eye gets fatigued. The eye quickly becomes fatigued and less sensitive to changes in the intensities of the tints. The eye should therefore be frequently rested by looking on the floor, or into the dark corner of a room.

There is also an appreciable difference in the sensitiveness of the two eyes for changes of colour. Hence, many shield or close the least sensitive eye, and use the most sensitive eye for comparing tints. The left eye, for example, is usually more sensitive than the right eye for variations in red tints, and hence the left eye is used for the colorimetric determination of iron. A similar remark applies to the titanium yellow. The eye requires more experience in detecting differences of shade with yellow tints, *e.g.*, in the titanium determination, than with many other colours.[1]

(2) *Unfavourable light.* The colours of the solutions might be compared with the light from a blue sky; light reflected from grey clouds, or clouds tinged with yellow or orange; light reflected from coloured objects; artificial light; or light which has been transmitted through a yellow fog. In each case, the effect of the incident light on the colour of the transparent solution is different. The source of the illumination is therefore of great importance in colorimetric work. In general, avoid artificial light and light tinged with yellow in, say, the titanium determination.

(3) *Differences in the concentration of the test and standard solutions.* The colour of many solutions is quite different in concentrated and in dilute solution. The solvent absorbs a certain amount of light; consequently, the concentration of the standard and test solutions should be the same. In the determination of iron there is a reaction between the coloring agent—$Fe(CNS)_3$—and the solvent water, so that the amounts of iron with different amounts of solvent will not be represented by the relation (1) above. Hence Duboscq's type of colorimeter is not suitable for the colorimetric determination of iron.

(4) *Changes in the standard solutions.* The standard solutions may deteriorate in strength, and may also be contaminated with impurities derived from, say, the glass bottles in which the solutions are kept, or from the atmosphere of the laboratory when the solutions are temporarily exposed. Such impurities may be fatal to the accuracy of determinations of ammonia, nitrites, and phosphates.

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[1] Constant errors in the comparison of colours can be eliminated by the method of substitution in which a solution of *known* strength is substituted in the test glass, after the unknown solution has been compared with the standard.

CHAPTER V.

FILTRATION AND WASHING.

A tremendous amount of time is consumed, often wasted, in the filtration and washing of precipitates for analytical work. Every device which will accelerate these fundamental operations, without interfering with their efficacy, must raise the efficiency of the laboratory.

§ 44. Filter Paper.

The purpose of filtration is to separate a solid from the liquid in which it is suspended. Filtration is usually effected by causing the liquid to pass through a medium which is porous enough to permit the passage of the liquid, and compact enough to retain the solid. Among the different filtering media in use are cotton-wool, sand, charcoal, crushed glass, glass-wool, asbestos pulp, paper pulp, platinum felt, asbestos paper,[1] and lastly, but most important of all, unsized paper—filter paper.

Filter paper should give no residue when distilled water or dilute hydrochloric acid is repeatedly passed through the paper, and the liquid then evaporated to dryness; a 10 per cent. aqueous solution of salicylic acid should give no perceptible coloration (showing the absence of iron); ammonium sulphide should not blacken the paper; nor should a dilute soda solution, which has been repeatedly passed through the paper, give a turbidity when neutralised with an acid (showing the absence of oils and fats).[2] Analysts, however, are not much troubled about the quality of their filter paper, because filter papers of remarkably good quality—almost pure cellulose—can be easily obtained.

Filter paper for analytical work should be kept in air-tight vessels. If the paper be exposed to laboratory fumes, the paper may absorb acid, ammoniacal or other fumes, and disturb certain determinations,[3] *e.g.*, determinations of the hardness of water. Paper which has been kept in an exposed place may subsequently liberate iodine from a solution of potassium iodide (free from iodate). Andrews too detected nitrites in filter paper which had been kept some time in a laboratory.

After filtration and washing, the paper is usually heated in a weighed crucible together with the solid until nothing but the ash of the paper remains, mixed with the calcined precipitate. The ash is weighed with the precipitate, and an allowance is made for the additional weight due to the ash of the filter paper. Owing to the fact that the precipitate has sometimes to be further investigated, it is an advantage to use filter papers with as little ash as possible. By treating the best filter paper with suitable acids, the manufacturer is able to reduce the amount of ash to a negligibly small quantity.[1] Indeed, the best filter papers behave as if they were almost pure cellulose—*i.e.* almost ashless.

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[1] A. Convert, *Chem. Centr.* (3), **16.** 850, 1885; A. Gruner, *Zeit. anal. Chem.*, **9.** 68, 1870; W. Johnstone, *Analyst*, **12.** 234, 1887.

[2] *Pharm. Post*, 252, 1896; L. Padé, *Bull. Soc. Chim.* (2), **47.** 243, 1887; W. Wicke, *Liebig's Ann.*, **112.** 127, 1859.

[3] H. R. Proctor, *Journ. Soc. Chem. Ind.*, **23.** 8, 1904; M. Mansier, *Journ. Pharm. Chim.* (6), **16.** 60, 1902; E. Mallinckrodt and W. N. Stull, *Journ. Amer. Chem. Soc.*, **26.** 1031, 1904; L. L. de Koninck, *Bull. Soc. Chim. Belg.*, **23.** 221, 1909.

Both Nos. 0 and 00, J. H. Munktell's Swedish papers, are excellent. My experience in quantitative work is confined to these, to C. Schleicher and Schüll's, and to M. Dreverhoff's filter papers. These manufacturers all supply papers of excellent quality. If not otherwise stated, Munktell's papers are recommended for the routine analyses in this book. The Swedish filter paper No. 0 has been washed in hydrochloric acid[2] to remove traces of iron, alumina, lime, and magnesia; No. 00 has been washed both in hydrochloric and hydrofluoric acids[3] to remove traces of silica,[4] as well as traces of iron, alumina, etc. Both brands of paper are quite satisfactory in general analytical work. No. 00 is rather expensive. It is suitable for the alumina filtrations where the silica must be kept as low as possible. Neither No. 0 nor No. 00 is suited for calcium oxalate and barium sulphate, which generally pass through the pores of these papers.[5] No. 0B has also been treated with hydrochloric acid, and is made rather thicker than No. 0. Consequently, it gives less trouble in the filtration of, say, calcium oxalate. A thin film of calcium oxalate will sometimes be found on the walls of a dried funnel which has been used with Nos. 0 or 00 papers for the filtration of the lime precipitate. No. 1F and No. 2 are unwashed Swedish filter papers which are suited for general work where a large number of filter papers of good quality are needed, and expenses must be kept down. No. 1F has rather a closer texture than No. 2, and does not filter so rapidly. The following Table XV. shows the amount of ash generally found in the different brands of unwashed paper, expressed in grams per paper:—

Table XV.—Amounts of Ash in Munktell's Swedish Filter Papers.
(Grams of ash per paper.)

Brand.	5·5 cm.	7 cm.	9 cm.	11 cm.	12·5 cm.	15 cm.
00	0·00001	0·00002	0·00003	0·00004	0·00006	0·00008
0	0·00006	0·00010	0·00017	0·00025	0·00033	0·00046
0B	0·00008	0·00014	0·00024	0·00035	0·00047	0·00065
1F	0·00014	0·00023	0·00038	0·00056	0·00073	0·00105
2	0·00018	0·00030	0·00051	0·00074	0·00095	0·00138

The amount of ash is so small that with, say, the No. 00 papers, and the smaller sizes of the other papers, the amount of ash can be neglected in routine work. If these papers have been used in a filtration, the amounts of ash will not be those given in the preceding table. The amount of ash furnished on burning a filter depends upon the nature of the liquid which has passed through the paper. A certain amount of fixed alkali, alkaline earth, and some salts are retained by the cellulose of the paper very tenaciously. If a neutral solution be passed through the paper, the salts may be retained by the paper, as in the case of the fixed alkalies.[1] Acids remove traces of mineral substances from the unwashed papers. Consequently the ash of unwashed papers may be reduced below the numbers given in the above table if they have been used for filtering acid solutions. In illustration, the following results (Table XVI.) were obtained for the ash of No. 00 filter papers which had been treated respectively with dilute sulphuric acid, and potassium hydroxide, and subsequently washed until the wash-water gave no reaction with neutral litmus solution. Ten of the 11-cm. papers were then incinerated, and the results divided by 10. The other sizes were obtained from these results by calculation.

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[1] For slight acidity of acid-washed filter paper, M. de la Source, *Ann. Chim. Anal.*, **2.** 82, 1897.

[2] U. Kreusler, *Zeit. anal. Chem.*, **24.** 81, 1885; *Chem. Ztg.*, **8.** 1323, 1884.

[3] P. T. Austin, *Chem. News*, **37.** 149, 1878.

[4] Not quite all—W. Lange, *Ber.*, **11.** 323, 1878.

[5] The smaller sizes of papers vary considerably in compactness. Some will retain these precipitates.

Table XVI.—Relation between the Filter Paper Ash and Liquid filtered.
(Grams of ash per paper.)

	5·5 cm.	7 cm.	9 cm.	11 cm.	12·5 cm.
Acid . .	0·000011	0·000019	0·000031	0·000047	0·000061
Alkali . .	0·000044	0·000071	0·000118	0·000176	0·000219

The inference is obvious. It is not sufficient to adopt the weight of the ash of the unused papers for a precipitate which has been isolated by the filtration of solutions containing salts which may be adsorbed by the filter paper. In exact work, the amount of ash in papers which have been treated with solutions resembling those used in the given filtration must be determined for a given precipitate. However, the ash of these papers in neither case need be considered in most analyses.[2]

C. Schleicher and Schüll's Nos. 589 and 590 correspond approximately with Munktell's Nos. 0 and 00 respectively. No. 589, "white ribbon," is an excellent paper with an ash but slightly greater than Munktell's No. 00, and hence negligible. It filters rapidly. No. 589, "black ribbon," has a more open texture than the corresponding "white ribbon," and filters more rapidly, but it is hopeless with finely divided precipitates like calcium oxalate and barium sulphate. The No. 589, "blue ribbon," is closer in texture than the corresponding "white ribbon." It filters more slowly, but will retain the finely divided precipitates better. It is useful for filtrations accelerated by gentle suction.[3]

To summarise, the three desiderata in a filter paper are: (1) porosity, to ensure rapid filtration; (2) sufficient compactness, to ensure complete retention of the solid; and (3) low amount of ash. The first and second qualities are antagonistic. It is important to *adapt the size of the filter paper to suit the precipitate to be washed. Use "rapid" (porous) papers for all precipitates which do not readily pass through the paper, and use the slow, compact papers only when absolutely necessary.*[4]

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[1] M. Mansier, *Journ. Pharm. Chim.* (6), **16**. 60, 1902.

[2] L. L. de Koninck (*Lehrbuch der qualitativen und quantitativen chemischen Analyse*, Berlin, **1**. 39, 1904) gives the following analysis, in round numbers, of the ash of Munktell's filter papers: SiO_2, 32; Al_2O_3, 15; Fe_2O_3, 9; MnO, 8; MgO, 11; CaO, 21; CuO, trace; alkalies, 2; SO_3, 2; P_2O_5, 0·2; Cl, trace.

[3] C. Schleicher and Schüll's No. 551 is black in colour, and used for filtering light-coloured sediments, minute traces of which can be easily detected on the black background. T. Fleitmann, *Zeit. anal. Chem.*, **14**. 77, 1875; W. Hempel, *ib.*, **14**. 308, 1875.

[4] A. Gawalovski, *Zeit. anal. Chem.*, **16**. 59, 1877; **18**. 246, 1879; **37**. 377, 1898; R. Fresenius and Caspari, *ib.*, **22**. 241, 1883; K. Kraut, *ib.*, **18**. 543, 1879; F. Mohr, *ib.*, **12**. 148, 1873; A. von Wich, *Viertel. prakt. Pharm.*, 8, 187, 1859; J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, **10**. 260, 1835; H. Uelsmann, *Dingler's Journ.*, **220**. 534, 1876.

§ 45. Filtration.

The *art* of quantitative analysis is largely dependent upon the skill exercised in transferring substances from one vessel to another without gain or loss.

Selecting the Funnel.—Do not use ribbed or guttered funnels for quantitative work. These often give trouble in washing. Finkener's funnel,[1] fig. 42, has a long capillary stem,[2] and it is supposed to have smooth walls inclined at an angle of 60°, so that when the paper is folded—four-ply—and opened out in the regular manner, it will fit close to the walls of the funnel.[3] The folding of papers with creases[4] to expose a large surface and prevent the paper lying close to the wall of the funnel is not recommended,[5] because (1) precipitate and paper are more difficult to wash; (2) there is a greater risk of breaking the paper; and (3) filtration is not so rapid as when the stem of the funnel is kept filled with liquid.

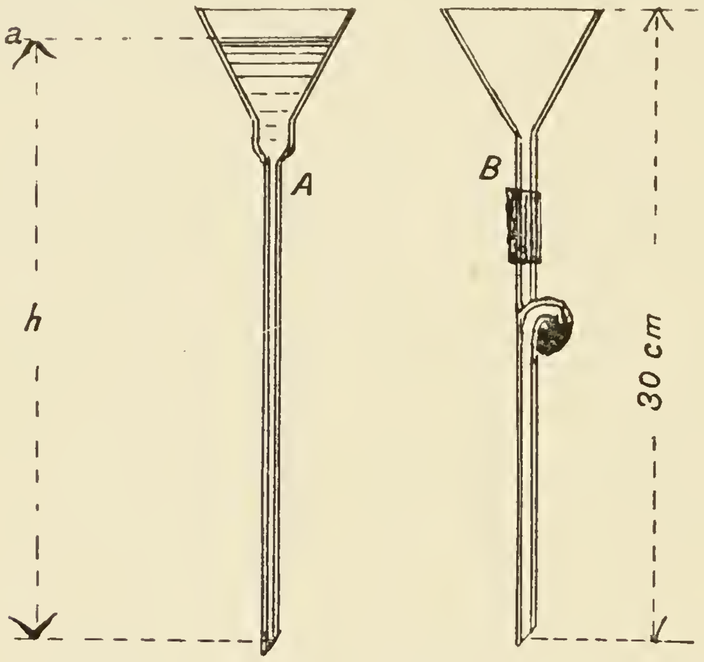

FIG. 42.—Long-stemmed funnels.

Fitting the Filter Paper in the Funnel.—When the paper is placed in the funnel it should not come nearer than half a centimetre to the top edge of the funnel, and on no account should the paper project beyond the funnel. The funnels best suited for the filter papers of different size are indicated below:—

Filter paper	5	7	9	11	12½	15	18	cm.
Funnel	2½–3	4	5	6½	7½	9	10	cm.

Place the paper in the funnel, wet the paper, and carefully bed it against the walls of the funnel. When the paper is filled with water, the stem of the funnel should fill with a column of water,[6] and air should not pass between the walls of the funnel and the paper as the paper empties. When the filter paper is properly bedded, water will flow through the paper quickly,[7] and filtration will usually proceed quite rapidly; at any rate, the paper is doing its best under the given conditions. The liquid in the filter paper is under a pressure equal to the weight of a column of liquid of the same diameter as the bore of the stem, and a height h, fig. 42, where a represents the level of liquid in the filter paper. Hence, in filtering, keep the paper filled to its greatest capacity in order to get a maximum value for h, which, in turn, corresponds with maximum velocity of filtration. If the bore of the tube be too wide, liquid will run down the sides of the tube and no pressure will be produced; while if the tube be too narrow, surface tension may prevent the flow of the liquid even when the funnel is full. A sharp tap on the filter stand will often start the flow.[1]

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[1] A. Gwiggnes, *Chem. Ztg.*, **27**. 889, 1903.

[2] F. Weil, *Zeit. anal. Chem.* **2**. 359, 1863; I. B. Cook, *Chem. News*, **27**. 261, 1873; **29**. 81, 1874; J. F. Kerr, *ib.*, **29**. 71, 1874; J. Piccard (*Zeit. anal. Chem.*, **4**. 45, 1865; G. Lunge, *Chem. News*, **13**. 23, 1866) proposed joining a narrow tube about 32 cm. long to an ordinary funnel by means of a piece of rubber tubing, as shown in fig. 42. Piccard's knot, as the tube is called, is much used in qualitative analysis, but is less suited for quantitative work. I have given the different types of funnel on the market a three months' trial in my laboratory, and found those indicated in fig. 42A best for quantitative work. "Funnel hangers" for supporting funnels on the sides of beakers are useful for short-stemmed funnels, but not for funnels with a long stem.

[3] If the slope of the funnel be not quite right, it may be necessary to alter the crease of the filter paper a little, so that the paper lies close to the walls of the funnel when opened out. If a very bad funnel is found in a batch, it may give more trouble than it is worth.

[4] C. E. Avery, *Chem. News*, **17**. 294, 1868.

[5] P. Hart (*Chem. Ztg.*, **32**. 1228, 1908) recommends the folded papers for fine sand and colloidal precipitates.

[6] The filling of the stem of the funnel is facilitated by keeping the stem free from grease by frequent treatment with the cleaning mixture of page 36; and also by making two constrictions in the stem. P. E. Raaschou, *Zeit. anal. Chem.*, **49**. 759, 1910.

[7] If the water does not flow through sufficiently rapidly, discard the paper, and use another.

Filter Funnel Stands.—The funnel should rest in a suitable stand with its stem vertical. Filter stands are generally made of hard wood—mahogany or teak. Stands are also made of metal and porcelain, with a metal rod, etc. The bevel of the opening through which the funnel passes should be the same as the funnel. For general work, the arm holding the funnel or funnels should be fitted with a screw so arranged that the funnels can be fixed at any desired height. In routine work, where a great number of filtrates may be in progress, with funnels all the same size, a larger stand with or without an arrangement for adjusting the height can be used with advantage.[2]

Inexperienced students are inclined to adapt the size of the filter paper to the bulk of the liquid to be filtered. In quantitative work, *the size of the filter paper must be determined by the magnitude of the precipitate, not by the bulk of the liquid to be filtered.* If too large a paper be selected, time is wasted in washing the paper, and it has just been pointed out that paper as well as precipitate has the property of retaining certain salts very tenaciously.

Transfer of Precipitate to Filter Paper.—The precipitate is usually allowed to settle before filtration.[3] The clear liquid should not be poured directly on to the funnel, but down a glass rod, where the stream is being directed towards the side, not the centre of the filter paper.[4] The receiving vessel for the filtrate should be so placed that the liquid running from the funnel does not fall into the centre, but down the side of the beaker so as to avoid any danger of loss by splashing. If desired, the receiving vessel for the filtrate can be covered by a glass plate with a hole at the side so as not to interfere with the position of the stem of the funnel. The funnel can also be covered with a clock-glass while the filtration is in progress. The object is to keep out dust.

If it be noticed while a filtration is in progress that too small a paper has been selected, so that the precipitate is likely to fill the paper more than half full, it is better to use another paper, and distribute the precipitate between the two papers. Ample room should be left for washing the precipitate. If the precipitate occupies more than two-thirds of the paper, difficulties will be encountered in the subsequent washing.

Policeman.—When the liquid has been transferred to the paper, it will generally be found that small portions of the precipitate remain adhering to the vessel.[1] These can usually be loosened by means of a *policeman*, which is made by covering the end of a glass rod with a tight-fitting piece of rubber tube. Pieces of rubber tube with solid ends are sold for the purpose, or they can be made from a piece of rubber tubing 3–4 cm. long by placing a little solution of caoutchouc in chloroform (or naphtha) within the rubber tubing at one end, and pressing the sides together between the jaws of a clamp[2] for a couple of days. The sealed end is then trimmed with a pair of scissors, and the open end is slipped on to a piece of glass rod, *a*, fig. 44, which fits the rubber tightly.[3] Specially rounded rubber cones, screwed to the end of ebonite rods, are sold for the purpose (*b*, fig. 44). The form fig. 44*a* is the better. A rubber finger-stall is usually more effective and quicker than the "policeman" in removing adhering precipitates from beakers—particularly if shallow beakers be in use. Care should be taken to select the Erlenmeyer's flasks used for precipitations with a bottom easily accessible to the "policeman."

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[1] Any dirt in the bore of these tubes is easily removed with a "tube cleaner" or a tobacco-pipe cleaner. E. Bauer (*Chem. Ztg.*, 12. 789, 1888) recommends a funnel with no stem at all for precipitates which filter with difficulty! His idea is to let the funnel dip in a vessel of water. By renewing the water occasionally, the precipitate is washed by diffusion. There is no advantage in this suggestion for general work. See also P. Blackman, *Chem. News*, 104. 30, 211, 312, 1911.

[2] F. Julian, *Journ. Anal. App. Chem.*, 3. 41, 1889; C. Mueneke, *Zeit. anal. Chem.*, 16. 228, 1877; G. H. Bostock, *Chem. News*, 57. 213, 1888; C. Simon, *Chem. Ztg.*, 9. 1870, 1885; A. A. Besson, *ib.*, 35. 408, 1911; P. Blaekman, *Chem. News*, 104. 30, 211, 1911.

[3] (1) Fine precipitates are then not so likely to run through the filter paper; and (2) the time occupied in standing ensures more complete precipitation with precipitates which form slowly, *e.g.*, magnesium ammonium phosphate, ammonium phosphomolybdate, potassium platinichloride, potassium cobaltinitrite.

[4] Do not stir up the liquid when the rod is returned to the liquid.

Washing the Precipitate.—The "policeman" is washed, and then the particles loosened by the "policeman" are washed from the beaker or flask into the filter paper by a jet of water blown from a wash-bottle. The nozzle of the wash-bottle is directed round and round the inside of the beaker. The final washing of the precipitate is effected by means of a jet of, say, water from a wash-bottle. The stream is first directed round the upper edge of the filter paper so as to wash downwards towards the apex of the cone; and the precipitate is collected as nearly as possible at the apex of the cone at the last washing. *The paper is never filled with water, and the precipitate is nearly always allowed to drain completely before adding fresh wash-water.* The washing is continued until a few drops of the filtrate collected in a test tube show the absence of the salts which are being washed from the precipitate.[4] The filtrate is usually required for the determination of another constituent, and, in consequence, as little of the filtrate as convenient must be employed in making the test, otherwise some of the filtrate will be lost. Six washings may suffice, but there is no fixed rule. Some precipitates retain the mother liquid more tenaciously than others, partly attracted by some kind of surface action, and partly entangled mechanically in the solid.

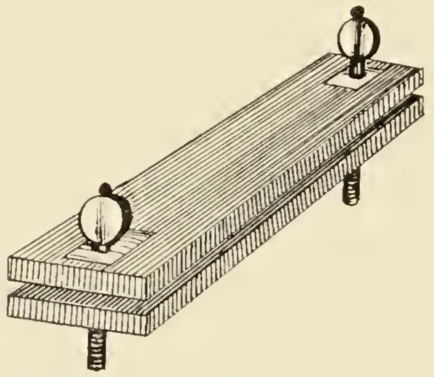

Fig. 43.—Clamp for making "policeman."

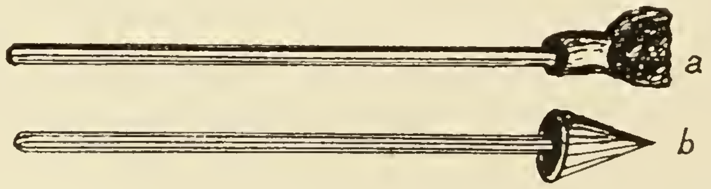

Fig. 44.—"Policemen."

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[1] If the particles cannot be scraped off, dissolve them in a suitable solvent and reprecipitate in a small beaker. In some cases, the particles need not be loosened, but left in the beaker. This is usually done when the precipitate is to be dissolved and reprecipitated, as is the case with the "alumina" precipitate in clay analyses. The beaker and the particles are washed as well as possible, and the solution of the precipitate on the filter paper is allowed to return into the beaker where the first precipitation was made.

[2] A clamp for the purpose is easily made from two pieces of wood, say, 30 cm. long, and 5 cm. by 2 cm. cross section. Holes are bored through each end to fit a pair of "sash screws," fixed as shown in fig. 43. The rubber tips are clamped by turning the thumb-screws.

[3] A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 31, 1908.

[4] In some cases, until a few drops evaporated on a piece of clean platinum foil give no residue.

It may seem that undue stress is laid upon manipulation. The great accuracy and skill with which a competent analyst does his work can only be acquired by a repetition of the same operations a great number of times. The student will probably notice that, as he gets more and more expert, a less volume of wash-water will be needed to wash a precipitate (page 97). There are some troublesome precipitates which at best require inconveniently large volumes of wash-water. When another constituent is to be separated from the filtrate, time is lost by the necessary evaporation, and the risk of loss during transfer from vessel to vessel is increased. In such cases it is best to change the receiver as soon as the liquid is filtered and washing commences. Collect the washings in an evaporating basin, and concentrate the washings by evaporation to a convenient volume. Mix the concentrated washings with the first filtrate. It is a good plan to regularly change the receiver as soon as washing commences, so that if the filtrate begins to get turbid towards the end of a washing, there will be no need to refilter all the liquid. Experience will soon teach what filtrates and washings may be safely collected in one receiving vessel.

§ 46. Wash-Bottles.

A great many types of wash-bottle have been suggested. The simpler types are generally best. Fig. 45 shows the forms most useful. *A* represents the ordinary cold-water bottle; *B*, the hot-water bottle. Both are fitted with rubber stoppers[1] and glass tubes. The neck of the hot-water bottle is wrapped round with thick string, flannel, cork, or some suitable non-conductor of heat.[2]

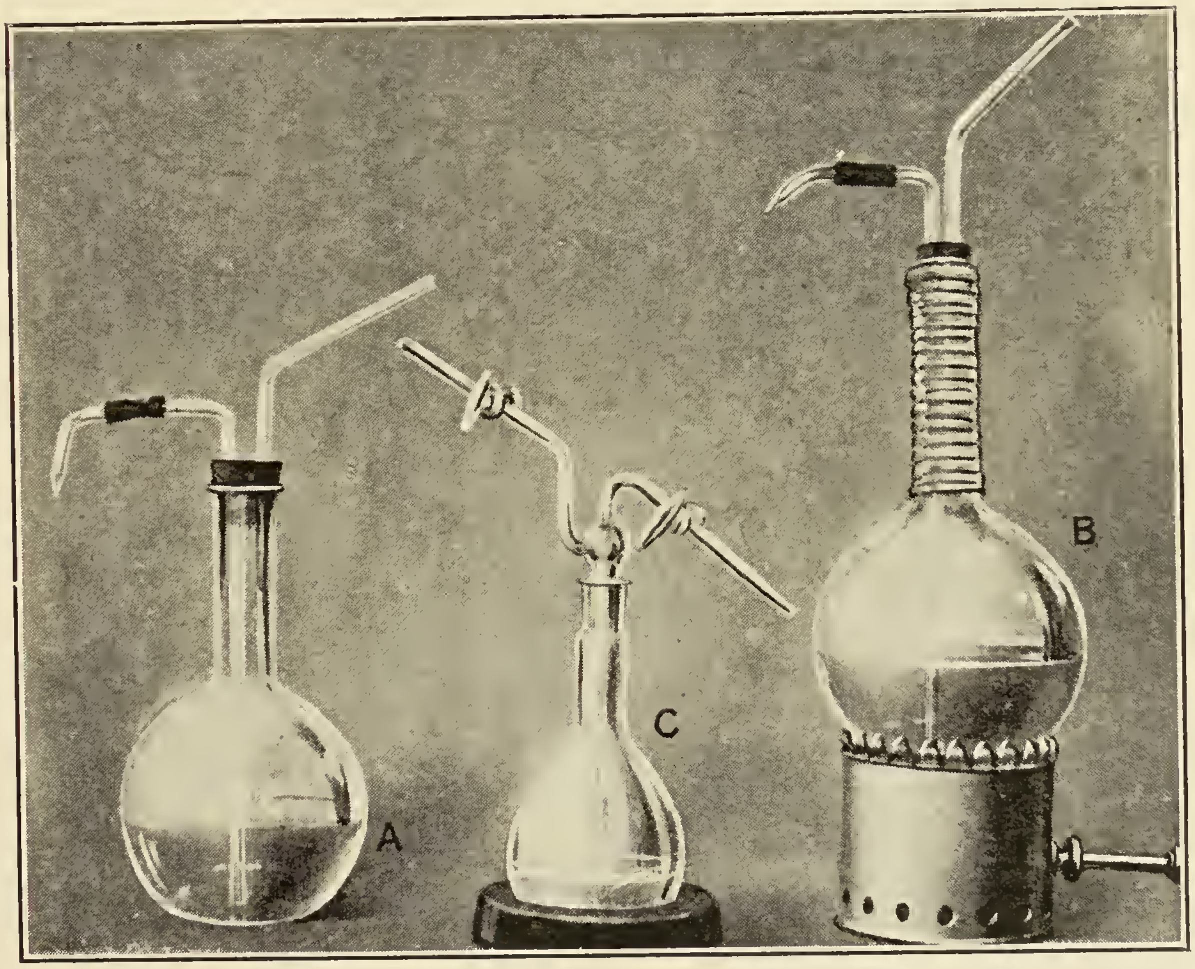

Fig. 45.—Wash-bottles.

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[1] There is a danger of contaminating the water with sulphuric acid derived from the sulphides—antimony—used in vulcanising the rubber. J. Pattinson and J. T. Dunn, *Journ. Soc. Chem. Ind.*, 24. 16, 1905.

[2] Asbestos paper is objectionable, because it is liable to flake off, and particles may thus get into the filter paper or filtrate.

The jets shown in the diagram are joined with pressure tubing. The jets can then be easily turned in any direction.[1]

A small Ostwald's heater,[2] shown at *B*, fig. 45, is useful for keeping the contents of the bottle warm. The stopper should rest on the neck while the bottle is being heated, in order to prevent steam escaping from the mouthpiece, and risking scalded lips or tongue. If the arrangement indicated below is used, there is no need for removing the stopper, etc., while the wash-bottle is being heated. It requires a little practice to regulate the "breath" so as to ensure hot steam is not sucked into the mouth. The student ought to learn to breathe through the nose while blowing from the mouth. The same action is used in working with the mouth blowpipe. Bottles for cold liquids may be made from thick glass,[3] but the hot-water bottles must not be too thick, or they may be fractured on heating. The "R" or the Jena glass type of flask is generally best.

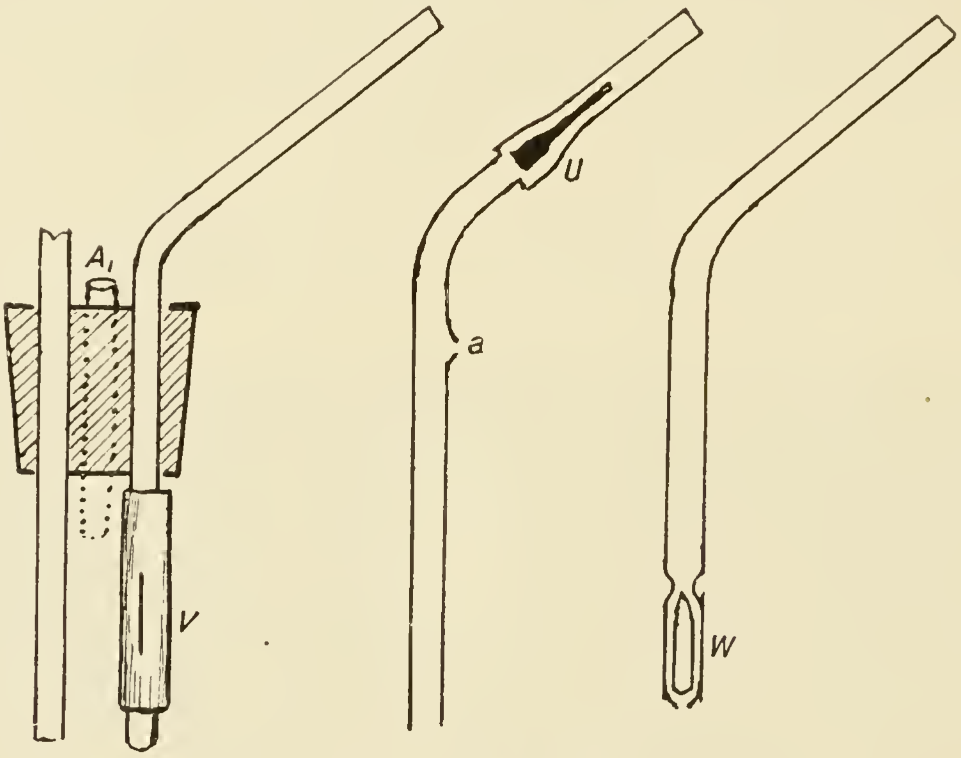

Fig. 46.—Valves for wash-bottle tubes.

Some prefer Erlenmeyer's flasks for wash-bottles. The wash-bottle *C*, with stoppered tubes, is used for alcohol and other volatile liquids, or for liquids which spoil on exposure to the atmosphere.[4]

Hot-water bottles, and wash-bottles containing ammonia water, ammonium carbonate, hydrogen, or ammonium sulphide solutions, and other unpleasant liquids, are best fitted with a special attachment, as shown in fig. 46. The part *A* is closed by the finger or thumb while blowing. The excess pressure closes the valve at *V*. The jet of liquid is stopped by withdrawing the thumb from *A*. The valve may be Griffin's (fig. 46, *U*), Bunsen's (fig. 46, *V*), Waters' (fig. 46, *W*), etc.[5] With Griffin's valve, a two-holed stopper suffices, since closing *a*, fig. 46, serves the same function as closing *A* in Bunsen's or Waters' valves.

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[1] G. Foord, *Chem. News*, **30**. 191, 1874; A. R. Leeds, *ib.*, **20**. 236, 1870; W. J. Land, *Amer. Chemist*, **3**. 221, 1874; A. Gawalovski, *Zeit. anal. Chem.*, **14**. 170, 1875.

[2] W. Ostwald, *Zeit. anal. Chem.*, **31**. 180, 1890; F. Muck, *ib.*, **28**. 611, 1889; J. Volhard, *Liebig's Ann.*, **285**. 330, 1895.

[3] W. Dittmar (*Chem. Ztg.*, **15** 1521, 1891) recommended nickel and copper bottles.

[4] For compressed-air wash-bottles, see W. C. Ferguson, *Journ. Amer. Chem. Soc.*, **16**. 149, 1894.

[5] For Bunsen's valve and some modifications, see page 188. J. J. Griffin, *Brit. Pat. No.* 464801, 1905; M. Stuhl, *Chem. Ztg.*, **21**. 396, 1897; E. Stroschein, *ib.*, **13**. 464, 1889; C. E. Waters, *Journ. Amer. Chem. Soc.*, **27**. 298, 1905; R. K. Meade. *ib.*, **19**. 581, 1897; F. M. Haldeman, *Journ. Anal. App. Chem.*, **2**. 301, 1888; L. M. Dennis, *Amer. Chem. Journ.*, **11**. 218, 1889; E. Jacob, *Zeit. anal. Chem.*, **5**. 168, 1866; T. Bayley, *ib.*, **18**. 295, 1879; E. Borgmann, *ib.*, **22**. 60, 1883 (stoppered tube on A); H. Dubovitz, *Chem. News*, **91**. 147 1905.

A Beutell's valve is easily made for this purpose, and it works better than Bunsen's. A piece of glass tubing 15 cm. long and 4–5 mm. bore is slightly contracted about 3 mm. from one end. Another piece of thin glass tubing, which fits loosely into the larger tube, with a free space about 0·5 mm. all round, is sealed and rounded off at one end. If the end be too tapered, it will be inclined to wedge tightly (fig. 46, *W*). The closed end is then fitted to the contracted part by grinding with emery and water, all the while rotating the tubes in one direction. If the joint appears tight after washing off the emery and sucking at *A*, fig. 47, dry the tube. Push the closed end of the narrow tube into a cork, and seal it off as near the closed end as possible, say 1 cm. away. The cork serves as a support for the closed end. The end must not be sealed too symmetrically, or it will be difficult, later on, to blow into the bottle. Bend the tube in the usual manner for the mouthpiece of a wash-bottle, as at *W*, fig. 46. With these instructions it will be easy to place the valve nearer the mouthpiece, and make it serve the same function as Griffin's valve.

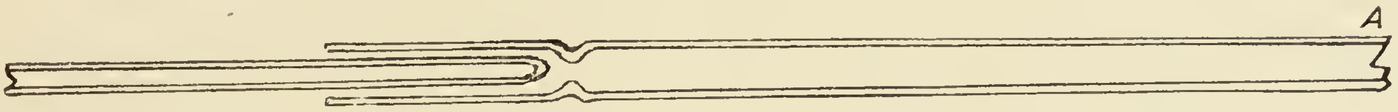

FIG. 47.—Making a valve for a wash-bottle.

Washing a Large Number of Precipitates.—When a number of precipitates have to be washed, the wash-bottle can be almost discarded, and a water supply —"bottle and syphon"—placed high above the working bench. The syphon tube is connected with a glass jet by a piece of rubber tubing sufficiently long to reach all the precipitates to be washed, and with a suitable tap for arresting or regulating the flow of the liquid used for washing the precipitates. If water be the washing fluid, arrangements can easily be devised for heating the reservoir. This arrangement is much more convenient than wash-bottles.[1]

§ 47. The Theory of Washing Precipitates.

Under ideal conditions the reagent employed for precipitations—the precipitant—should form a precipitate of definite composition, which is very sparingly soluble, or rather insoluble, in the mother liquid and washing fluids. Any excess of the precipitating agent should be readily removed from the precipitate by washing (or by ignition). The precipitating agent should not introduce any substance likely to interfere with the precipitation of other constituents from the filtrate later on. Again, the precipitate should be compact, easily filtered and washed. Few processes satisfy all these desiderata, and an important part of analytical chemistry is to know what conditions favour and what conditions hinder the separation and purification of a given precipitate. There are, however, a few general principles of such wide applicability that they should be carefully studied.

Colloidal and Fine-grained Precipitates.—In general, the finer the grain of the precipitate, the greater the quantity of contaminating salts retained by the wet precipitate. Fine-grained precipitates expose a large surface of separation between the solid and solution. The salts appear to be retained by a kind of surface attraction which is called, for convenience, adsorption. Hence, fine-grained precipitates are more difficult to wash clean than coarse-grained precipitates.[2] Colloidal gelatinous precipitates like ferric and aluminium hydroxides are in an extremely fine state of subdivision, and, in consequence, they are most difficult to wash clean. Such precipitates may require ten to twenty washings, and then not be so clean as a coarse-grained crystalline precipitate after two or three washings.

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[1] G. E. Boltz, *Journ. Amer. Chem. Soc.*, **33**. 514, 1911.

[2] The term "coarse-grained precipitate" of course does not mean aggregates formed by the clotting of a number of fine grains.

Again, fine-grained precipitates, like newly precipitated barium sulphate, lead sulphite, calcium oxalate, and silver chloride, are particularly liable to pass through the filter paper, while coarse-grained precipitates give no trouble. Hence, the analyst employs various artifices in order to coagulate or to crystallise gelatinous and amorphous precipitates. Among the more important means of effecting these changes are :—

(1) The grain size can be frequently increased by allowing the precipitate to stand in the mother liquid for some time. This, for instance, is the case with lead chromate, antimony oxychloride, manganese ammonium phosphate, sodium antimoniate, stannic hydroxide, calcium oxalate, silver chloride, metallic sulphides, barium sulphate, etc.[1]

(2) Precipitates produced in hot solutions are often coarser-grained than precipitates produced in cold solutions. The boiling of precipitates in a fine state of subdivision may lead to the flocculation of a large number of the fine particles into a relatively small number of coarse grains. Zinc sulphide, barium sulphate, and manganese ammonium phosphate may be cited in illustration.

(3) The flocculation of a precipitate which separates in a colloidal condition is frequently effected by the salts present in the mother liquid. When these salts have been almost removed, during the later stages of the washing, the coagulated precipitate sometimes passes to a colloidal or gelatinous condition, and it may then give a turbid filtrate, or become so slimy as to be almost impermeable to the washing liquid. In such cases it is necessary to wash the precipitate, not with pure water, but with a solution of an acid or salt which will prevent the deflocculation of the precipitate, and which can be easily removed by drying or ignition. Acids can only be used with precipitates of an acid nature, *e.g.*, washing titanium hydroxide with acetic acid (page 208); and with precipitates insoluble in even strong acids, *e.g.*, silver chloride, which is washed with dilute nitric acid (page 652). Usually, we have to depend upon the ammonium salts—nitrate, sulphate, chloride, and acetate.[2] For instance, washing the "alumina" precipitate with ammonium nitrate (page 183). The ammonium salt is volatilised when the precipitate is calcined.[3]

Adsorption of Salts by Precipitates.—On account of the adsorption of a certain amount of salt with colloidal precipitates, such as occurs, for instance, in the ammonia precipitate, the adsorbed salts cannot be all removed by washing, and there are many reasons for supposing that all precipitates carry down with them, that is, adsorb, substances from the solution in which they are formed. The adsorbed salts cannot always be removed by washing. The wash-water may show no indication of the impurities so retained by the precipitate. Thus,

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[1] G. Watson, *Chem. News*, 63. 109, 1891.

[2] R. Bunsen, *Liebig's Ann.*, 106. 13, 1858. Salts of polyvalent metals and alkaline earths give the best results, but these, with the exception of mercury, are excluded because they would remain with the precipitate after ignition. Mercury salts can only be used in a limited number of cases on account of secondary reactions. Ammonium salts are perhaps least effective, but they are usually the best we can do. See R. G. Smith, *Journ. Soc. Chem. Ind.*, 16. 872, 1897; N. Pappada, *Zeit. Chem. Ind. Kolloide*, 9. 233, 1911.

[3] See page 363. Sometimes precipitates which are difficult to filter clear can be satisfactorily filtered if a little recently ignited kieselguhr (J. P. Ogilvie, *Journ. Soc. Chem. Ind.*, 30. 62, 1911), or china clay (F. Watts and H. A. Tempany, *ib.*, 27. 53, 1908), be added to the mixture—*e.g.*, for lead sulphite. The device is particularly useful when the filtrate is alone wanted, or when the precipitate is to be afterwards dissolved in a solvent which does not attack the clay or silica.

Warington[1] found that ferric hydroxide precipitated by potassium carbonate only lost two-thirds of this salt by a washing which would have removed 0·0069th part of a salt not adsorbed by the precipitate. The same observer records the adsorption of various salts by aluminium and ferric hydroxides. It is therefore frequently advisable to dissolve the precipitate in a suitable solvent, and reprecipitate. The objectionable impurity divides itself in a definite ratio between the precipitate and mother liquid. A relatively large amount may be retained by the precipitate during the first precipitation, but on a second precipitation, when only that amount of salt which was retained by the first precipitate is in solution, the partition of the undesirable salt between the precipitate and the solution in the given ratio means that a relatively small amount of impurity will be retained by the second precipitate. Two, possibly three, precipitations will generally remove appreciable amounts of the objectionable impurity from the precipitate. For instance, aluminium and ferric hydroxides, manganese ammonium phosphate (page 374), zinc sulphide (page 364), nickel and cobalt sulphides (page 388), etc. Suppose that the first precipitate retains 0·01th part of the objectionable salts, while 0·99th part is removed by filtration. The second precipitate will contain 0·01th of 0·01th of the salt; the third precipitate, 0·000001th of the salt. Thus, repeated reprecipitation will soon carry the amount of impurity outside the range of the balance.[2]

These facts also lead us to conclude that, if a small quantity of a substance A is to be separated from a large quantity of a substance B, it is generally better to precipitate A rather than precipitate B. The loss of A through absorption by B makes the "error of experiment" greater than if some of B be lost through absorption by A.

Amount of Fluid required for Washing Precipitates.—A rather important question has to be decided in washing precipitates. Is a relatively small number of washings with large volumes of liquid more effective than a relatively large number of washings with small volumes of liquid? Suppose that a precipitate be allowed to drain on a filter paper, and that the precipitate exercises no physical or chemical action on the salts in solution in the mother liquid.[3] Let the volume of the mother liquid retained by the moist precipitate be represented by v c.c. Add V c.c. of water to wash the precipitate. The total volume of liquid will be $(v+V)$ c.c. Let this drain on the filter paper. The moist precipitate retains v c.c. of the $v+V$ c.c Otherwise expressed, the precipitate on the first draining retains $\frac{v}{V+v}$ c.c. of the mother liquid. After the first washing, again add V c.c. of water and let the precipitate drain. The moist precipitate retains, on the second draining, a volume $\frac{v}{V+v}$ of the $\frac{v}{V+v}$ c.c. of the mother liquid. Hence, the precipitate retains:

First draining $\left(\frac{v}{V+v}\right)$ c.c. of the mother liquid;

Second draining $\left(\frac{v}{V+v}\right)^2$ c.c. of the mother liquid;

nth draining $\left(\frac{v}{V+v}\right)^n$ c.c. of the mother liquid.

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[1] R. Warington, *Journ. Chem. Soc.*, 21. 1, 1868; P. Jannasch and T. W. Richards, *Journ. prakt. Chem.* (2), 39. 321, 1889; Ed. Schneider, *Zeit. anal. Chem.*, 10. 425, 1882; T. W. Richards, *ib.*, 46. 189, 1903; *Proc. Amer. Acad.*, 35. 377, 1900; K. Scheringa, *Pharm. Weekblad*, 48. 674, 1911.

[2] In the case of some "rare earth" separations, where the ratio is relatively large, a great number of precipitations—fractional precipitations—may be required to effect the separation. W. Crookes, *Chem. News*, 54. 131, 1886; K. Scheringa, *Pharm. Weekblad*, 48. 674, 1911.

[3] The assumption is rarely justified, but this does not affect the principle under discussion.

In order to understand what these expressions symbolise, it is advisable to take a numerical example. Suppose that a precipitate, which retains each draining, $v=1$ c.c. of the mother liquid, is to be washed until it retains but 0·000001 c.c. of the mother liquid. In that case, after the nth washing, we have

$$\left(\frac{1}{1+V}\right)^n = 0{\cdot}000001.$$

If $n=6$, V is nearly 6 c.c., and if $n=4$, V is nearly 18 c.c. This means that the precipitate will be washed as clean with six washings ($n=6$), using 6 c.c. of water ($V=6$) each time, as with four washings ($n=4$), using 18 c.c. ($V=18$) each time. In the former case, 36 c.c. of wash-water pass through the filter paper, and in the latter case, 72 c.c. of water pass through the filter paper. Hence, in this particular case, half as much water is needed to wash the precipitate six times with 6 c.c. of water each time as is needed to wash the precipitate four times with 18 c.c. of water each time. Hence, *the washing of a precipitate is more efficiently performed by the frequent application of a small volume of water than by using a relatively large volume of water applied a small number of times.* It is here assumed that the precipitate is allowed to drain before it is refilled with washing liquid.[1] This theory of washing precipitates was developed by Bunsen, in 1868.[2]

Horsley deduces from his experiments:

1. To keep down the volume of the wash-water, keep the quantity of liquid on the filter paper small throughout.
2. The time required for filtration cannot be quickened or delayed by any change in the method of adding the wash liquid, provided the upper edge of the filter paper be attended to.
3. To minimise the drudgery of filtration, make each addition as large as possible, and allow the precipitate to drain; but the time of washing will not be affected.

§ 48. Bunsen's System of Accelerated Filtration.

The long-stemmed funnels I have just recommended give very good results in routine work, but a considerable amount of time can be saved by using suction, as recommended by Bunsen.[3] The Swedish filter papers recommended above will not bear much suction. They will burst near the tip. In consequence, a small perforated platinum filter cone, fig. 48, is placed in the funnel to help the paper to bear the pressure.[4] The filter cone is first placed in the funnel, and the paper is bedded on to cone and funnel. If the paper be not properly bedded to both cone and funnel, it will inevitably be torn as soon as strong suction sets in. The funnel is fixed in the neck of a stout-walled filtration flask, F, figs. 49 and 56, by means of a rubber stopper. The filtration flask is

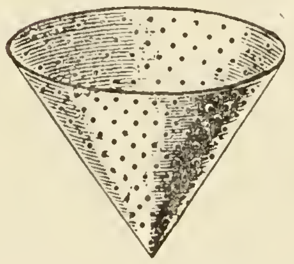

Fig. 48.—Filter cone.

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[1] In washing by decantation with boiling water, T. W. Das (*Chem. News*, **101**. 169, 1910) recommends transferring the precipitate, after each decantation, to the filter, washing out the precipitate into a beaker, adding fresh water, and repeat. This ensures the better removal of the mother liquid, and more rapid washing.

[2] R. Bunsen, *Liebig's Ann.*, **148**. 269, 1868; G. F. Horsley, *Chem. News*, **87**. 237, 1903.

[3] R. Bunsen, *Liebig's Ann.*, **148**. 269, 1868; *Zeit. anal. Chem.*, **8**. 174, 1869; E. C. Hildebrand, *Chem. News*, **34**. 57, 1876; C. Jones, *Journ. Anal. App. Chem.*, **1**. 383, 1887; V. Kreusler, *Chem. Ztg.*, **8**. 1324, 1885. For filtration under pressure, T. Feller, *Zeit. anal. Chem.*, **3**. 325, 1864.

[4] A. Gawalovski, *Zeit. anal. Chem.*, **23**. 372, 1884. R. S. Dale, *Chem. News*, **20**. 128, 1869, for copper cone. See, and for funnels with a perforated inner wall, C. Nickles, *Journ. Soc. Chem. Ind.*, **6**. 134, 1887; J. de Mollins, *Zeit. anal. Chem.*, **19**. 334, 1880.

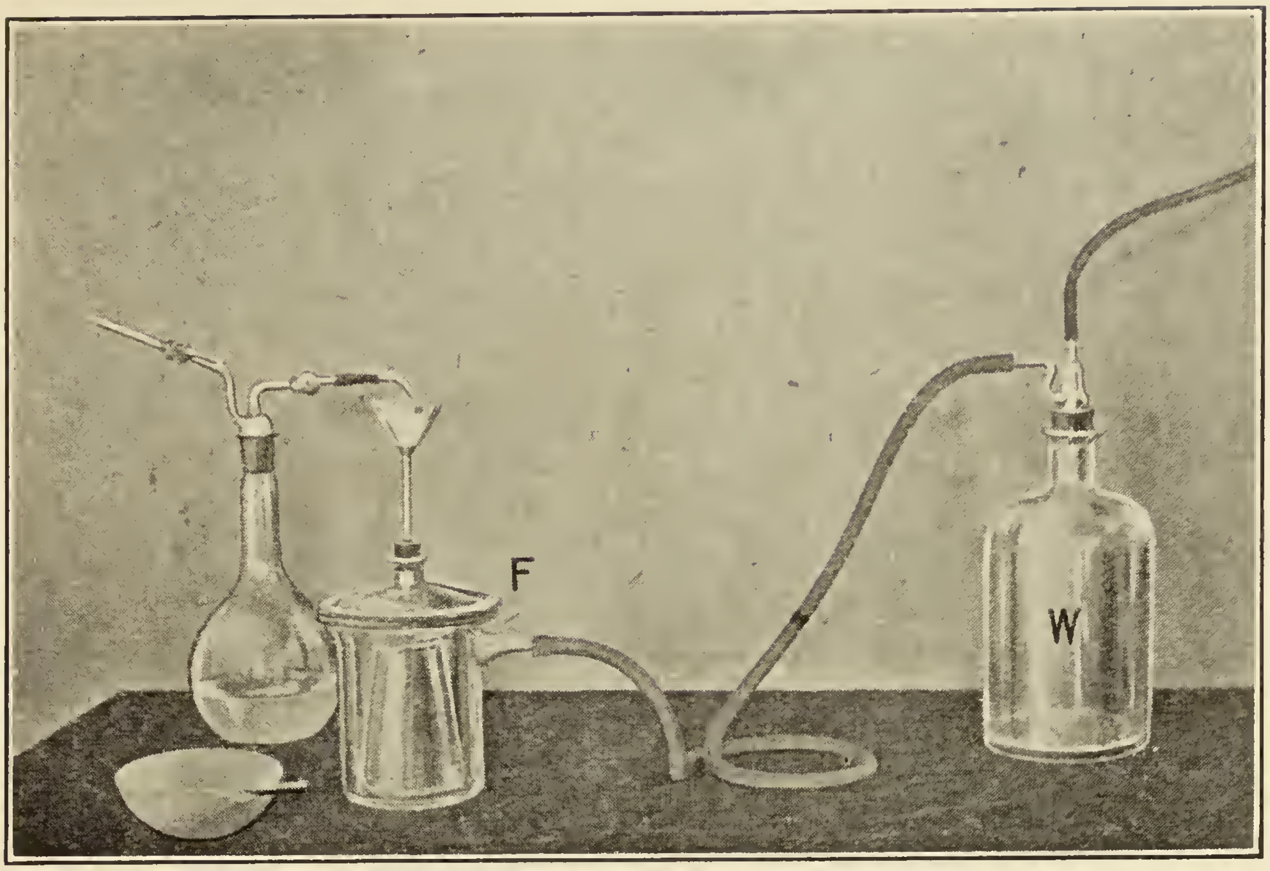

Fig. 49.—Filtration with platinum cone and Witt's flask.

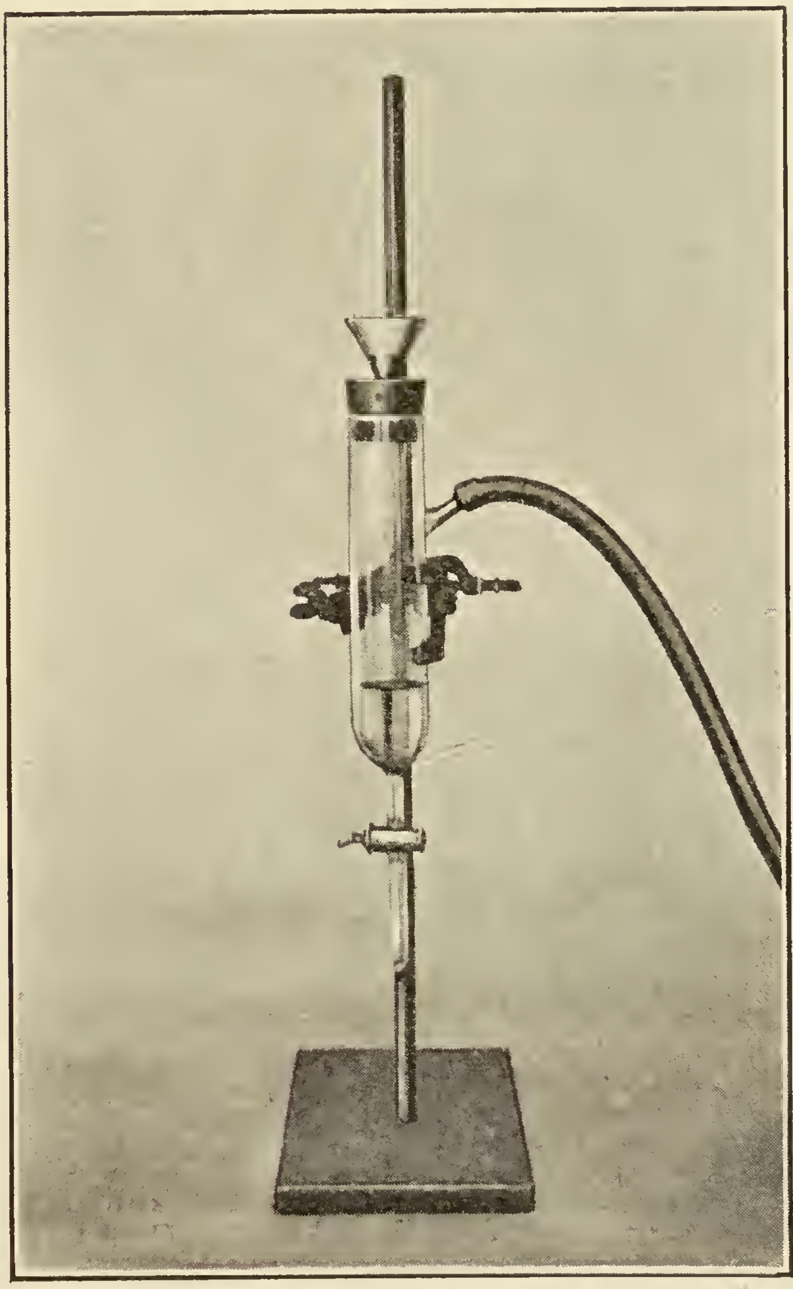

Fig. 50.—Zöpfchen's filtering tube.

connected with a Woulff's bottle or similar flask *W*, and this in turn with the suction pump. The bottle between the filtration flask and the pump prevents a back-rush of water into the filtration flask when the pump is stopped. The connections are made with stout-walled rubber tubing which will not collapse under the diminished pressure. If the filtrate is to be used afterwards, I prefer Witt's filtration jar, *F*, fig. 49.[1] In this, the filtrate is collected in a beaker as indicated in the diagram. Zöpfchen's[2] filtration tube, fig. 50, is useful when small quantities are under investigation, and in other special cases. Instead of a platinum cone, filter papers with toughened tips are useful when the pressure is not too great.[3] These are made by immersing the tip of the folded paper in nitric acid (sp. gr. 1·42) for a few moments, and then thoroughly washing the paper with water. These papers are C. Schleicher and Schüll's No. 580. The same firm makes toughened filter papers, No. 575. The small sizes (4 or 5·5 cm.) can be used in place of the platinum cone. The toughened paper cone can be pierced in a number of places near the tip, with a fine needle.[4]

In filtering and washing precipitates under diminished pressure, as a rule, do not allow the precipitate to drain, but add more liquid before the former liquid has run through. If the precipitate be allowed to drain, as recommended for ordinary filtration, channels or fissures sometimes form in the precipitate. The wash-water then simply runs through the channels without coming in contact with the bulk of the precipitate.

§ 49. Tared Filter Papers.

Some precipitates, when collected on a filter paper, cannot be ignited with the paper on account of volatilisation, decomposition, etc. These cases require special treatment. In some cases the filter paper is separated from the precipitate and ignited separately. In other cases the filter paper is dried at, say, 100° or 120° and weighed.[5] The precipitate is then collected and washed on the filter paper in the usual manner. The paper and contents are then partially dried in the funnel (so that the paper and contents can be removed without tearing the paper), placed in the weighing bottle, and later dried at the desired temperature, say, 110° or 120°. The paper is very hygroscopic, and it should be protected from the atmosphere while being weighed. Consequently, the paper may be folded and placed between a pair of weighed watch-glasses, *e*, fig. 3; in weighing tubes, *f*, fig. 3; or in Reinhardt's weighing bottle,[6] fig. 51. Some papers, after use, are liable to disintegrate and break if folded; in that case, either Reinhardt's bottle or Koninck's weighing funnel, *B*, fig. 52, can be employed. The latter is made specially thin, and it fits on to a ground tube *G* in the stopper of the filtration flask *F*. After the funnel has been used for filtering, it is placed on the tripod *A*, which acts as a ground stopper. The funnel and contents are then dried, the ground cover *C* placed on the funnel, and the whole cooled and weighed. Instead of the funnel,

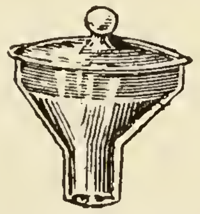

Fig. 51.—Reinhardt's weighing bottle.

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[1] O. N. Witt, *Chem. Ind.*, 510, 1899; A. R. Leeds, *Chem. News*, **23**. 177, 1871; **21**. 236, 1870; A. Burgemeister, *Zeit. anal. Chem.*, **28**. 676, 1889; F. Allihn, *ib.*, **26**. 721, 1887.

[2] H Zöpfchen, *Chem. Ztg.*, **25**. 1008, 1901; H. S. Bailey, *Journ. Amer. Chem. Soc.*, **31**. 1144, 1909.

[3] E. E. Francis, *Journ. Chem. Soc.*, **47**. 183, 1885; J. F. Stoffart, *Journ. Anal. App. Chem.*, **4**. 1, 1890; C. R. C. Tichborne, *Pharm. Journ.* (3), **2**. 881, 1871.

[4] M. H. Cochrane, *Chem. News*, **32**. 80, 1875.

[5] C. Gilbert, *Rep. anal. Chem.*, **1**. 264, 1882; J. L. Smith, *Chem. News*, **31**. 55, 1875.

[6] C. Reinhardt, *Zeit. angew. Chem.*, **2**. 61, 1889; L. L. de Koninck, *ib.*, **1**. 689, 1888.

a filter tube *b* also can be fitted on to the same joint *G* in the stopper of the filtration flask *F*. The filter tube *b* has a glass cap *c* and plug *a* for use during the weighing.

If an allowance is to be made for the action of the liquid being filtered on the paper, it will be necessary to treat a second paper with the clear filtrate and find the effect on the weight of the paper after the paper has been washed and dried. The loss or gain in the weight of the empty paper, by the treatment, represents the effect of the solution on the filter paper containing the precipitate, and an allowance must be made accordingly.[1] The following is the best plan:—Two filter papers are cut the same size, and one is weighed against the other. The difference in weight is marked with a pencil on the heavier. Each filter paper is placed on a funnel. The solution to be filtered is poured through the one, and the filtrate is poured through the second paper. Similarly, duplicate the washings. The two filter papers are dried in the ordinary manner. In weighing, the empty paper is placed on the right pan as a tare to the other, and due allowance made for the excess in the weight of the one paper over the other.[2]

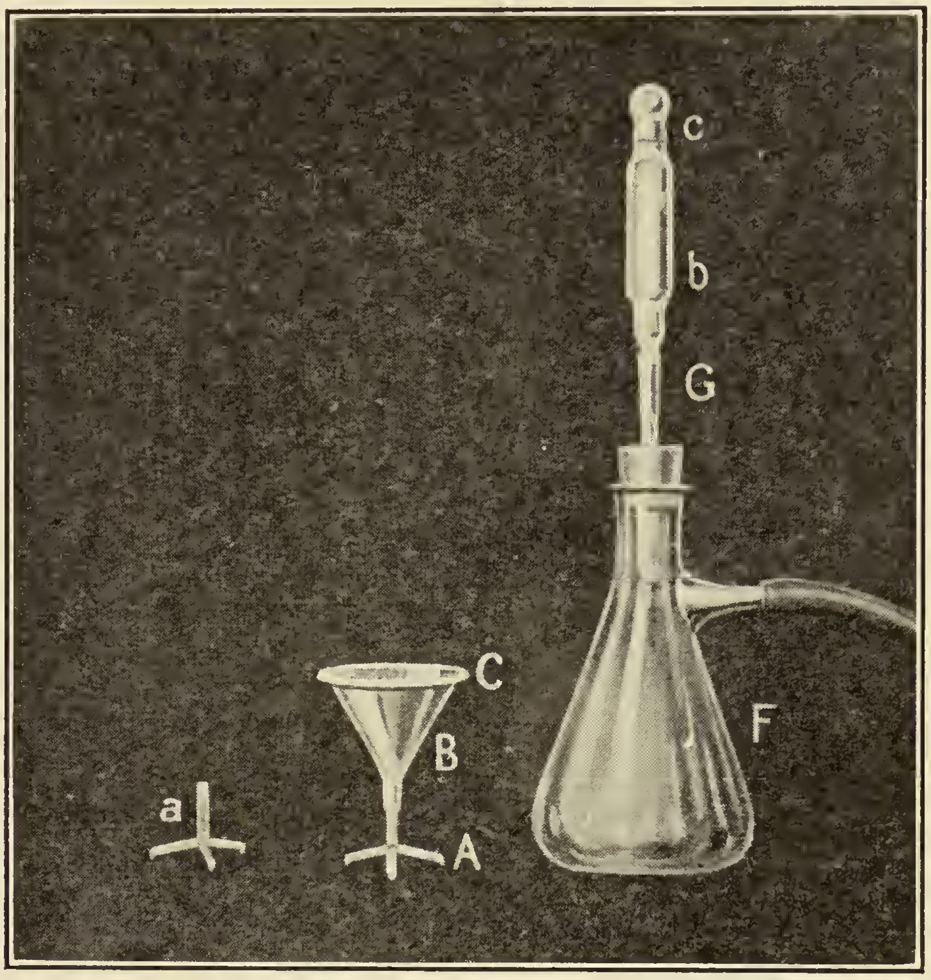

Fig. 52.—Koninck's filtration apparatus.

A certain amount of judgment is required in using the different weighing tubes. For example, the Koninck's apparatus weighs about 50 grms. The precipitate may weigh 0·005 grm. The apparatus is thus 10,000 times heavier than the precipitate! The large surface exposed by the glass may introduce a small error which is relatively large in comparison with the substance being weighed. In general, the greater the difference between the weight of the precipitate and the weight of, or rather the surface exposed by, the apparatus, the greater the percentage error affecting the determination. It is therefore best to keep the weighing apparatus as small as possible. Processes involving the use of tared filter papers are rapidly falling out of use. The weighing of precipitates by means of tared filter papers will soon be obsolete.

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[1] If any solid matter should escape the first paper, and be retained by the second, the work would probably be stultified. This is the objection to placing the second paper below the first in the funnel while the liquid is being filtered, and separating the papers, later on, for weighing.

[2] C. Rüdorff, *Zeit. angew. Chem.*, **3**. 633, 1890; *Chem. News*, **66**. 25, 1892.

§ 50. Filtration Tubes.

Instead of using tared filter papers, substances which are injured by burning filter papers may be filtered through cotton-wool,[1] asbestos,[2] felt cloth,[3] glass-wool,[4] gun-cotton, etc. Thus, a tube shaped as indicated in fig. 53, *A*—E. Allihn's tube — may be packed first with glass-wool (*a*), then with, say, asbestos (*b*). Some precipitates are liable to clog if the asbestos be packed in too thick a layer—for instance, manganese oxide precipitated by potassium chlorate. In that case, some prefer a small plug of glass-wool (*a*), followed by a 0·6 to 0·7 cm. layer of calcined Calais sand (*b*),[5] with or without a thin layer of asbestos over the sand. Several different ways of packing have been suggested, and several different forms of filter tube.[6] For instance, the tube may be stoppered at each end—Jannasch's filter tube, fig. 204, page 653—or the tube may be capped at one end and stoppered at the other, as *a b c*, Koninck's tube, fig. 52. In Fresenius' filter tube there is a constriction *a*, fig. 53, *B* ; and the tube may have a bulb in the region of the packing, fig. 53, *C*, which is Gibbs and Taylor's tube. In Mason's filter tube, *D*, fig. 53, the stem is separate from the body of the tube, so that, when in position, it forms a ledge on which a perforated "filter plate" can rest. The stem is rather longer than the body of the tube, so that it can be used to eject the filter bed, etc.

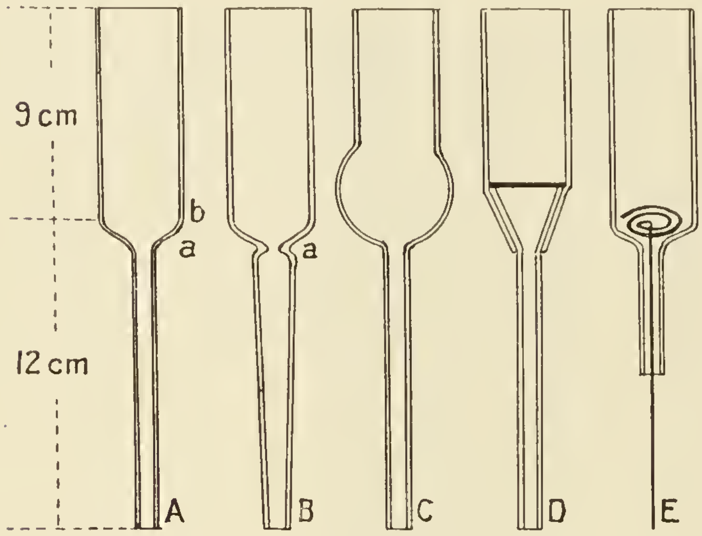

Fig. 53.—Filtration tubes.

In the analysis of iron where the carbon is separated as insoluble matter, the carbon is filtered in a tube of various forms—*e.g.*, a platinum tube with a perforated removable disc which is covered with asbestos before filtration ; a glass tube with a platinum spiral,[7] fig. 53, *E*, covered with long fibre and ignited asbestos ; etc. The carbonaceous matter is afterwards dried and burnt in a current of oxygen, or by the wet combustion process. Several other modifications are in use.[8] Thus, the carbon may be collected directly in a platinum boat fitted with a suitable bottom, and holder for the filtration flask.

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[1] A. B. Clemence, *Journ. Anal. App. Chem.*, **1.** 273, 1887.

[2] See Gooch's crucibles, page 104.

[3] R. Frühling and J. Schuz, *Zeit. anal. Chem.*, **13.** 146, 1874.

[4] It is well to remember that the glass-wool is often made from lead glass, and may give up some lead to acid solutions. F. Muck, *Zeit. anal. Chem.*, **19.** 140, 1880 ; L. Blum, *ib.*, **31.** 292, 1892 ; F. Stolba, *ib.*, **17.** 79, 1878 ; R. Böttger, *Notizblatt*, **34.** 3191, 1884 ; M. Battandier, *Journ. Pharm. Chem.* (4), **30.** 55, 1880.

[5] C. M. Sargent and J. K. Faust, *Journ. Amer. Chem. Soc.*, **21.** 287, 1899 ; *Chem. News*, **79.** 158, 1899. S. Kern, *ib.*, **38.** 157, 1878, platinum tubes with asbestos packing. P. Weisskopf, *Dingler's Journ.*, **206.** 243, 1872, felted glass-wool packing.

[6] R. Fresenius, *Zeit. anal. Chem.*, **8.** 154, 1869 ; O. Lohse and P. Thomaschewski, *ib.*, **39.** 158, 1900 ; W. Gibbs and E. R. Taylor, *Amer. J. Science* (2), **44.** 215, 1867 ; F. Allihn. *Journ. prakt. Chem.* (2), **22.** 56, 1880 ; F. Soxhlet, *ib.* (2), 21, 231, 1880 ; A. Goske, *Chem. Ztg.*, **22.** 21, 1898 ; *Ber.*, **32.** 2142, 1899 ; J. S. C. Gray, *Chem. News*, **22.** 165, 1895 ; H. P. Mason, *ib.* **91.** 180, 1905 ; T. Macfarlane, *Analyst*, **18.** 73, 1895.

[7] T. M. Drown, *Tech. Quart.*, **20.** 552, 1891.

[8] See Shimer's filter tube, page 620.

§ 51. Filtration through Perforated Discs and Funnels.

In 1870, Carmichael[1] proposed a different system of filtration from those which precede. Carmichael's plan was to keep the solution in a platinum dish in which the precipitate is to be finally weighed. A disc of filter paper was placed against the lower perforated surface of the vessel, whose interior was connected with the suction apparatus. The liquid, wash-water, etc., was sucked from the vessel, and the precipitate was prevented from leaving the vessel by the filter paper. Casamajor[2] modified this by using a kind of perforated false bottom with an aspirator, and covering the upper surface of the perforated plate with a disc of filter paper or asbestos pulp. Any liquid poured into the dish could then be filtered by suction through the perforated bottom. Sauer[3] suggested the use of flat discs of platinum gauze; and Grosjean, perforated platinum discs, in an ordinary funnel. A piece of filter paper, rather larger than the disc, was supposed to be placed on the upper surface of the perforated disc. The paper was wetted and pressed close against the disc and funnel, so as to form a watertight joint all round the disc. The chief objection to the use of these discs for quantitative work arises from the fact that only part of the precipitate collects on the disc; part collects on the funnel, whence it can only be removed with difficulty. In order to keep the discs horizontal, Smith[4] soldered a platinum rod to the under side of the disc. When the rod was dropped into the stem of the funnel, the disc was in a horizontal position. The so-called Witt's filter plates[5] are made of glass or porcelain, rather larger in diameter on the upper side; otherwise they resemble Grosjean's discs, and Kaehler added the vertical rod as previously suggested by Smith. Kaehler's filtration discs are also made with a groove to take a rubber band between the disc and the funnel, thus ensuring a better joint between plate and funnel. Kaehler's discs are also made of porous earthenware, asbestos, or alundum (fused alumina) without perforations and of different porosities.[6] In Hirsch's[7] funnels (fig. 54) the disc is an integral part of the funnel.

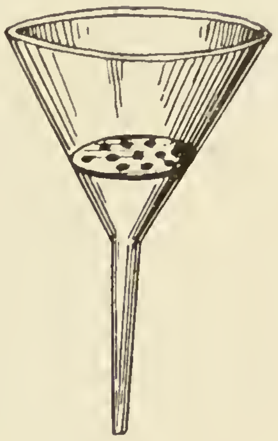

FIG. 54.—Hirsch's funnel.

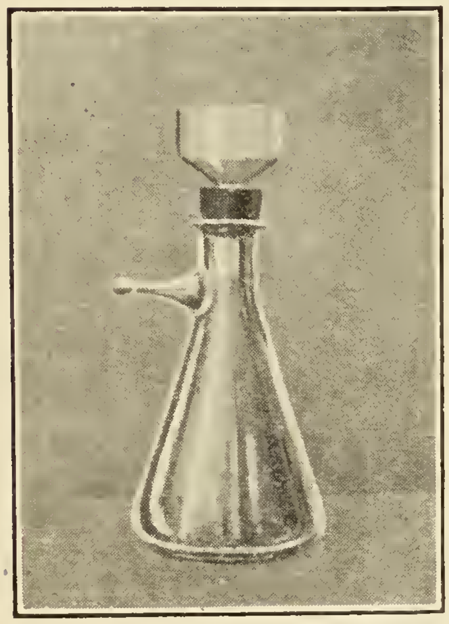

FIG. 55.—Büchner's funnel.

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[1] H. Carmichael, *Zeit. Chem.* (2), **6**. 481, 1870 ; *Chem. News*, **24**. 213, 1871 ; W. Jago, *ib.*, **33**. 54, 1876 ; C. Ville, *ib.*, **30**. 200, 1874 ; J. P. Cooke, *Proc. Amer. Acad.*, **12**. 125, 1877 ; W. A. Puckner, *Journ. Amer. Chem. Soc.*, **15**. 710, 1893 ; R. Frühling and J. Schulz, *Zeit. anal. Chem.*, **13**. 146, 1874 ; L. W. Bahney, *Met. Chem. Eng.*, **10**. 737, 1912.

[2] P. Casamajor, *Amer. Chem.*, **5**. 440, 1875 ; **6**. 124, 1876 ; *Chem. News*, **32**. 33, 45, 183, 1875 ; **45**. 148, 1882 ; **46**. 8, 1882 ; **53**. 194, 248, 1886 ; *Journ. Amer. Chem. Soc.*, **3**. 125. 1881 ; **8**. 17, 1886 ; K. Zulkowsky, *Zeit. anal. Chem.*, **17**. 198, 1878 ; **18**. 459, 1879 ; **22**. 173, 1883. For reversed filtration, see also A. Wildenstein, *ib.*, **1**. 432, 1862 ; M. C. Lea, *Amer. J. Science* (2), **42**. 379, 1866 ; E. Fleischer, *Chem. News*. **19**. 169, 1869.

[3] A. Sauer, *Zeit. anal. Chem.*, **14**. 312, 1875 ; B. J. Grosjean, *Journ. Chem. Soc.*, **16**. 341, 1879 ; *Chem. News*, **39**. 182, 1879 ; **45**. 107, 1882.

[4] J. C. Smith, *Amer. Chem. Journ.*, **1**. 368, 1879 ; S. L. Penfield and W. M. Bradley, *Amer. J. Science* (4), **21**. 453, 1906 ; *Chem. News*, **94**, 293, 1906.

[5] O. N. Witt, *Ber.*, **19**. 918, 1886 ; M. Kaehler, *Zeit. anal. Chem.*, **33**. 63, 1894 ; *Journ. Amer. Chem. Soc.*, **16**. 58, 1894 ; C. H. Piesse, *Chem. News*, **28**. 198, 1873 ; R. Warington, *Zeit. anal. Chem.*, **25**. 354, 1886, used lead plates for tartaric acid. A. Bornträger, *Ber.*, **19**. 1690, 1886.

[6] R. C. Benner and W. H. Ross, *Journ. Amer. Chem. Soc.*, **34**. 51, 1912.

[7] R. Hirsch, *Chem. Ztg.*, **12**. 340, 1888 ; E. Büchner, *ib.*, **12**. 1277, 1888 ; **13**. 95, 1889 ; E. Murmann, *Zeit. anal. Chem.*, **50**. 742, 1911.

In the different forms of the so-called Büchner's funnels (fig. 55) the disc may or may not be permanently fixed, but the walls of the funnel above the disc are vertical. The sloping sides of the funnel below the disc narrow rapidly. The disc presents a more extended surface than in Hirsch's funnel. These are all different modifications of the one principle. Some of these funnels are valuable auxiliaries in preparation work. They are used with perforated rubber stoppers, filtering flask, and suction, as illustrated in fig. 56. For other forms see page 630.

§ 52. Gooch's Filtration Crucibles.

In 1878, F. A. Gooch[1] proposed to filter certain liquids by suction through a bed of asbestos resting on the perforated bottom of a crucible, **Gooch's crucible.** The crucible, *c*, is fitted into a large rubber ring, *b*, fig. 56, which, in turn, fits tightly into the top of a glass adapter, *a*, resembling a "thistle-headed funnel." The glass adapter is fitted into a filtration flask. F. Gooch's crucibles are used so much in analytical work that their preparation and use must be described in some detail.

1. *Preparation of the Asbestos.*[2]—There are several varieties of asbestos on the market. The long-fibre "silky" crysolite asbestos gives the best results, since it does not pack so closely as many of the less suitable varieties, and, in consequence, it filters most rapidly. Place a 10's brass wire sieve, bottom upwards, on a sheet of paper. Rub a handful of asbestos roughly over the sieve so as to break the asbestos into smaller fragments which pass through the sieve.[3] Collect that which remains on the sieve into another bundle, and repeat the operation until sufficient fibre has passed through. Next remove the dust and the fine powder by placing the material on a 30's lawn and agitating the mass while water is poured over the sieve. When the water which passes through has lost its "milky" appearance, and seems quite clear, transfer the washed asbestos to a beaker or flask and boil for about half an hour with hydrochloric acid (1 : 4). Now wash the asbestos by pouring it over a perforated funnel—Hirsch's or Büchner's—fitted with a piece of filter paper. Mix the washed asbestos with water, and the asbestos emulsion so prepared may be kept in a bottle ready for use.

2. *Packing the Crucible with Asbestos Felt.*—A platinum or glazed porcelain crucible with a perforated bottom of the required size is fitted into an adapter shaped as shown in fig. 56, *a*.[4] This is mounted in a perforated rubber stopper which fits the neck of the filtration flask *F*. A piece of rubber *b*, made for the purpose, is placed over the mouth of the funnel, and the crucible *c* fitted into the rubber collar. J. J. Griffin & Sons (Kingsway) make perforated rubber stoppers which enable Gooch's crucible to be fitted directly into the filtration flask (fig. 57).[5] Pour enough asbestos emulsion into the crucible to give a layer of asbestos 1 to 2 mm. thick. The suction must not be too great, or the asbestos will pack too

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[1] F. A. Gooch, *Proc. Amer. Acad.*, **13**. 342, 1878; *Chem. News*, **37**. 181, 1878; G. C. Caldwell, *Journ. Amer. Chem. Soc.*, **13**. 105, 1891; T. Paul, *Zeit. anal. Chem.*, **31**. 537, 1892; *Chem. News*, **67**. 8, 1893.

[2] P. Casamajor, *Chem. News*, **47**. 17, 1883; T. Paul, *Zeit. anal. Chem.*, **31**. 543, 1902; W. P. Barba, *Journ. Anal. App. Chem.*, **5**. 596, 1891; **6**. 35, 1892; *Chem. News*, **65**. 101, 1892; P. A. Kober, *Amer. Chem. Journ.*, **41**. 430, 1909.

[3] Or scrape the fibrous asbestos down with a knife.

[4] T. W. Richards (*Journ. Amer. Chem. Soc.*, **31**. 1146, 1909) has added a funnel-like flange to the top of the ordinary Gooch's crucible in order to facilitate washing. H. Vollers (*Chem. Ztg.*, **29**. 1088, 1905) has a raised cylinder with perforated walls in place of the flat bottom of the ordinary Gooch's crucible. The designer claims that this renders the crucible less liable to get blocked than the ordinary flat-bottomed crucibles.

[5] W. R. Forbes, *Chem. News*, **105**. 27, 1912.

tightly and the subsequent filtration will be slow.[1] Place the perforated disc—filter plate—upon the asbestos, and pour more emulsion into the crucible, so as to make a layer 0·5 to 1 mm. thick, as indicated in section, fig. 58. Run water through the crucible until no asbestos fibres run through. If the water which has run through the crucible be held in a good light, the floating asbestos fibres can be readily seen. Usually, $\frac{1}{4}$ to $\frac{1}{2}$ litre of water suffices. Dry the asbestos and weigh. Again pass $\frac{1}{4}$ to $\frac{1}{2}$ litre of water through the crucible, dry, and weigh again. If the weight be the same as before, the crucible is ready for use.

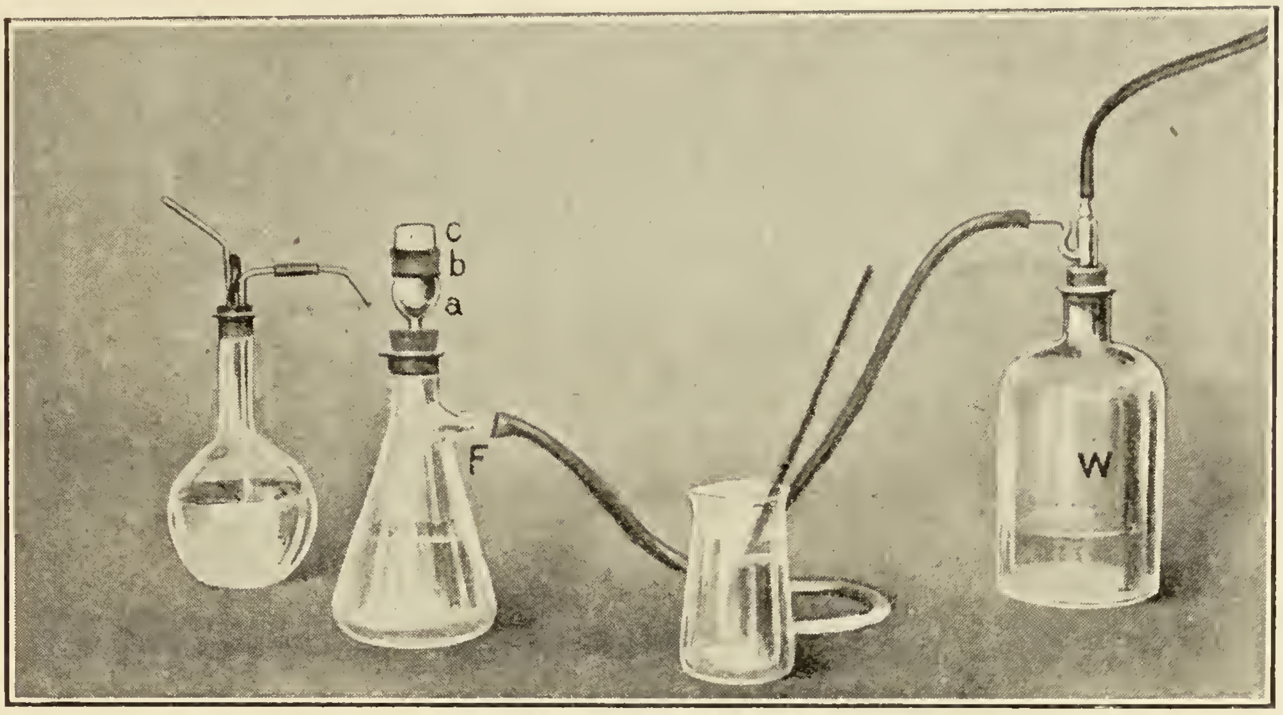

Fig. 56.—Filtration with Gooch's crucible.

3. *How to use the Gooch Crucible.*—The dry and weighed crucible is mounted over a filter flask or Witt's jar (figs. 49 and 56). The liquid to be filtered is passed through the crucible, and the precipitate washed as if the crucible were a filter paper and funnel. When the precipitate has been washed and the crucible dried, the whole is weighed. The increase in weight represents the weight of the precipitate. If the precipitate is to be ignited, it must be placed within a larger crucible or in a Gooch's saucer (fig. 59) and heated, at first gently, and then at the desired temperature. The ignited crucible is cooled and weighed in the usual manner.

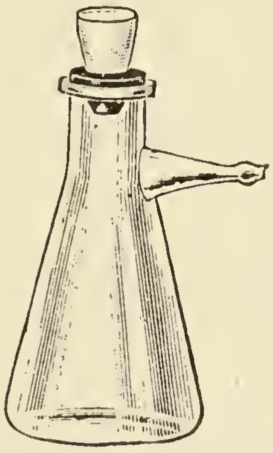

Fig. 57.—Fitting Gooch's crucible in filtration flask.

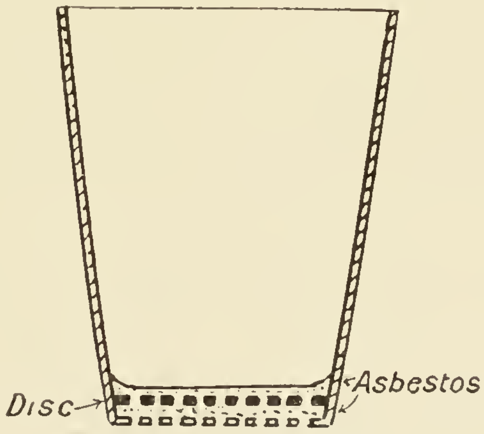

Fig. 58.—Section of Gooch's crucible.

The same crucible can be used for a number of determinations of the same substance. When the collection of precipitates in the crucible becomes too large, the upper part can be removed, or the crucible recharged, and used as indicated above.

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[1] It is often a good plan to let the joint between the crucible and rubber leak a little, or insert a regulating tap between *F* and *W*, or *W* and the pump. F. H. Wolff, *Neues Jahrb. Pharm.*, 36. 65, 1871.

4. *Sources of Error.*—Asbestos dried at 100°–110° to a constant weight may lose between 0·001 and 0·002 grm. of moisture on ignition. It is therefore necessary, when the weight of an ignited precipitate is to be determined, to dry or ignite the packed crucible the same length of time and at the same temperature as that intended for the precipitate.[1] It is important, also, to remember that calcined asbestos may absorb appreciable amounts of alkali not removed by washing. Most of the asbestos of commerce is also slightly attacked by water and feebly acid solutions. If the crucible is prepared as indicated above, there is no danger of losing asbestos during the washing of a precipitate.

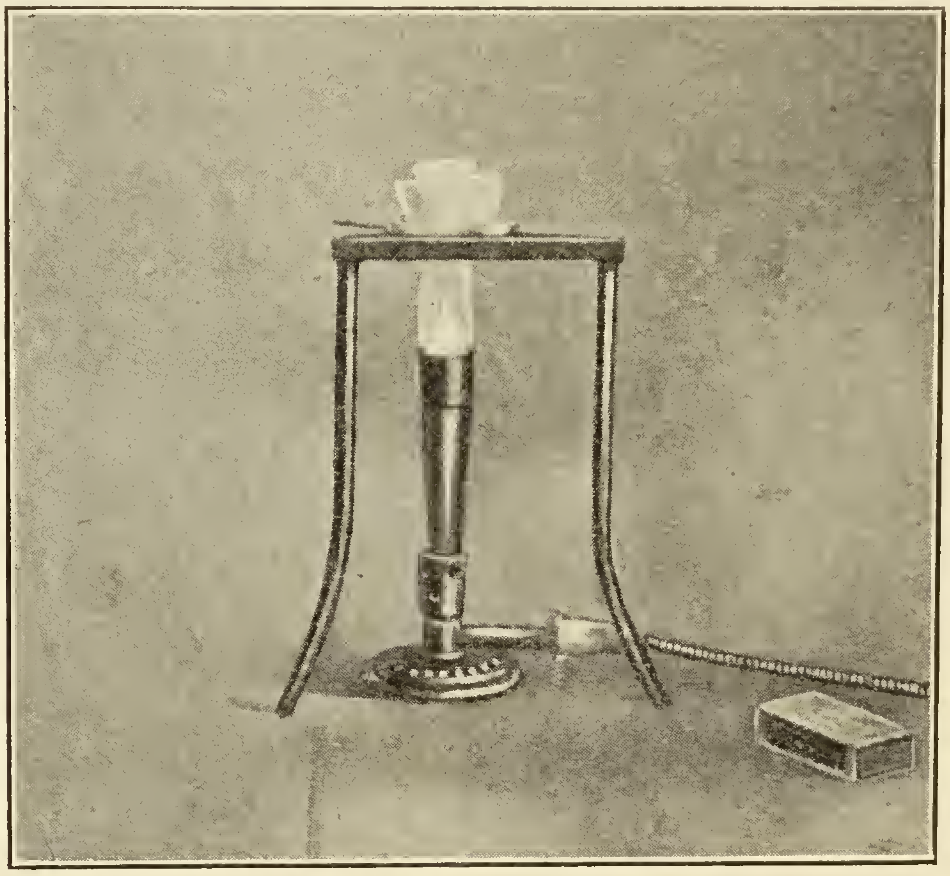

FIG. 59.—Ignition of Gooch's crucible.

The filter tube is usually preferable to the Gooch's crucible when it is necessary to heat the precipitate in a current of gas.[2]

§ 53. Gooch's Crucibles packed with Soluble or Volatile Felts.

The Gooch's crucible has deservedly won a permanent place in general analytical practice. It is exceptionally valuable when precipitates are to be redissolved from the felt after washing (*e.g.*, sodium titanate in hydrochloric acid); when a mixed precipitate is to be separated into parts by appropriate solvents (*e.g.*, washing antimony sulphide free from sulphur by carbon disulphide); separation of sulphides soluble and insoluble in alkaline sulphides, and generally when the desired solvent attacks filter paper and not asbestos. In some cases, the felt, after the action of the solvent, has to be separated from the solution by filtration and washing. In that case, Gooch[1] proposed packing the crucible with anthracene instead of asbestos. The anthracene emulsion[2] is made by moistening anthracene with alcohol and then shaking the mass with water. The emulsion is used as if it were asbestos,[3] with due regard to its special properties. To remove the anthracene from a precipitate, stand the crucible in a small beaker,[4] add enough of the solvent—benzene for preference—and gently warm the vessel by immersing the beaker in hot water.[5] Wash the precipitate with the solvent, then with alcohol, and finally with water if necessary. The volatility of anthracene enables it to be removed by volatilisation in some cases where it is not wanted—say, when a barium sulphate precipitate is to be treated with concentrated sulphuric acid. Crucibles with anthracene felt are not much used, and they must give way to the more convenient Munroe's crucible.[6]

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[1] Or find the amount of moisture retained by the dry Gooch's crucible, and make the necessary allowance when the precipitate is weighed. G. Auchy, *Journ. Amer. Chem. Soc.*, **22.** 46, 1900; H. Theile, *Zeit. öffent. Chem.*, **7.** 388, 1901; K. Windisch, *Chem. Centr.*, **75.** ii. 1621, 1905; M. Austin, *Amer. J. Science* (4), **14**, 156, 1902.

[2] E. Murmann (*Monats. Chem.*, **19.** 403, 1898) has described a modified Gooch's crucible in which the precipitate can be dried and heated in a current of gas—*e.g.*, lead sulphate, barium sulphate, zinc, manganese, copper, and antimony sulphides, etc. They are rather expensive and fragile.

§ 54. Gooch's Crucibles packed with Platinum Felt—Munroe's Crucible.

C. E. Munroe[7] proposed platinum sponge in place of the asbestos in Gooch's crucible, and crucibles so packed have so many applications, not possible with the asbestos-packed crucibles, that they are bound to win a permanent place in general practice. Although Munroe's crucible was suggested in 1888, its merits have only recently attracted serious attention. The main objection to Munroe's crucible is its cost—the platinum felt is packed in a platinum crucible; but Brunck[8] has made a similar crucible with Royal Berlin porcelain, and "burned" the felt into the glaze so that it cannot be detached without the application of force, or overfiring. Brunck's crucible will bear a red heat if the temperature be raised gradually.

1. *Preparation of the Platinum Felt.*—A concentrated solution of chloroplatinic acid is treated with ammonium chloride in slight excess. The resulting precipitate of ammonium platinichloride is washed several times with water, and finally with alcohol. The excess of alcohol is poured off as soon as the ammonium platinichloride has settled.

2. *Packing the Crucible.*—A perforated platinum crucible, with small and numerous perforations, is placed upon several layers of filter paper, and pressed firmly on the paper while the alcohol-moist mass of ammonium platinichloride is

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[1] F. A. Gooch, *Proc. Amer. Acad.*, **20**. 390, 1885; *Chem. News*, **53**. 234, 1886.

[2] Anthracene is insoluble in water and aqueous solutions of salts, alkalies, and dilute acids; but soluble in benzene, carbon disulphide, etc. Anthracene volatilises at 213°. Naphthalene might be used in place of anthracene.

[3] If the anthracene of commerce be too coarse, dissolve it in hot water, and precipitate by cooling with water.

[4] Wagner's filter tube (M. Wagner, *Pharm. Ztg.*, **52**. 766, 1907) has a stopcock and perforated glass disc fused into a filter tube. By closing the stopcock, and pouring in the solvent, a precipitate can be kept immersed in a small quantity of the solvent as long as desired.

[5] Note the inflammability of the solvent. No naked flame must be near.

[6] In some special cases, an emulsion of filter paper or gun-cotton is used The paper pulp filters very slowly. Böttger recommended gun-cotton in place of asbestos in cases where the precipitate is to be ignited in an oxidising atmosphere (H. N. Warren, *Chem. News*, **61**. 63, 1890; F. Stolba, *Zeit. anal. Chem.*, **17**. 79, 1878).

[7] C. E. Munroe, *Journ. Anal. App. Chem.*, **2**. 241, 1888; *Chem. News*, **58**. 101, 1888; H. Neubauer, *Zeit. anal. Chem.*, **39**. 501, 1900; W. C. Heraeus, *Zeit. angew. Chem.*, **13**. 745, 1900; P. Bernhardt, *Chem. Ztg.*, **32**. 1227, 1908; O. Brunck, *ib.*, **33**. 649, 1909; W. O. Snelling, *Chem. News*, **99**. 229, 1909; *Journ. Amer. Chem. Soc.*, **31**. 456, 1909; O. D. Swett, *ib.*, **31**. 928, 1909; T. W. Richards and A. Staehler, *ib.*, **29**. 623, 1907; F. Zerban and W. P. Naquin, *ib.*, **30**. 1456, 1908; F. A. Gooch and F. B. Bayer, *Amer. J. Science* (4), **25**. 249, 1908; M. M. Brewer, *George Washington Univ. Bull.*, **5**. 79, 1906; *Chem. Eng.*, **5**. 261, 1906; H. J. F. de Vries, *Chem. Weekblad*, **6**. 816, 1909.

[8] O. Brunck, *Chem. Ztg.*, **33**. 649, 1909.

poured in until it is filled, say, to a height of 0·25 or 0·5 cm.[1] The alcohol will be rapidly absorbed by the filter paper upon which the crucible is being pressed, and at the end of a few moments the surface of the salt in the crucible will suddenly appear "dry," showing that the excess of alcohol has been absorbed by the filter paper. The filter paper will prevent the salt running through the perforations at the bottom. The crucible is then removed from the filter paper, and a uniform layer of ammonium platinichloride should cover the bottom of the crucible. Warm the crucible in a steam oven until the alcohol has all volatilised. Place the cap and cover on to the crucible, and gradually warm the crucible until the ammonium platinichloride has all decomposed. The temperature may then be raised to dull redness. Let the crucible cool.

The bottom of the crucible should be covered with a continuous and uniform layer of platinum sponge, but generally the sponge will be found to have withdrawn, more or less, from the sides of the crucible, and to be interrupted by several cracks. Press the mass gently with the finger, or with a glass rod with a flattened end, so that the cracks are pressed together and a continuous layer of the platinum sponge is spread over the bottom of the crucible. If, however, the layer is not quite continuous, use fresh chloroplatinic acid to fill up the cracks, and to "patch" the layer of platinum sponge. The cracks, etc., may be so bad that it is advisable to remove the platinum sponge by means of a spatula, and start again. When the crucible is covered with a uniform layer of platinum sponge, it is ready for use.[2]

Munroe recommends rubbing the platinum sponge with a glass rod at this stage in order to smooth out the mat and remove cracks. This compresses the mat and burnishes its surface. By gently rubbing all parts of the mat until the surface becomes considerably burnished, the smooth, polished surface so obtained has many advantages, even though the porosity of the felt is greatly reduced.

The felt prepared by the above directions, due to Snelling, is said to be 100 times more porous than one of asbestos. It also retains the finest precipitates without the difficulties of turbid filtrates or clogging of the felt presented by asbestos felt in filtering barium sulphate and calcium oxalate. There is also no danger of contaminating the filtrate with silica, alumina, iron oxide, magnesia, and lime, as is the case with asbestos felt. The crucible is used for filtering and washing, like the regular Gooch's crucible, page 104.

One special advantage of Munroe's crucible is that the precipitate can be removed by means of appropriate solvents, and the crucible dried and weighed ready for the next determination.

In illustration, the following results may be quoted from Munroe's paper :—

	grms.
Platinum crucible alone	30·6744
Crucible and felt, first ignition	31·0607
Crucible and felt, second ignition	31·0607
Crucible and felt, third ignition	31·0607
Crucible, felt, and calcium oxalate	31·5385
The same after treatment with HCl, etc.	31·0609
Second treatment with hydrochloric acid	31·0608
Crucible felt, and barium sulphate	31·4403
After treatment with conc. H_2SO_4	31·0640
Second treatment with conc. H_2SO_4	31·0609

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[1] Snelling recommends placing a circular piece of fine platinum wire gauze of suitable size in the bottom of the crucible before pouring in the ammonium platinichloride. The felt is then tougher and less easily injured, and also less liable to crack and curl.

[2] Snelling recommends the addition of two or three drops of chloroplatinic acid to the platinum felt in the crucible. The porosity of the felt will cause the solution to distribute itself throughout the whole mass. On ignition, the chloroplatinic acid will be decomposed with the separation of platinum. The platinum which is so formed appears to cement the particles of platinum sponge together and to the walls of the crucible, so that the felted mass is toughened.

The crucible can be used over and over again for hundreds of analyses, unless careless handling makes the introduction of a new felt necessary. After weighing, the crucible is inverted to remove part of the precipitate, and the remainder is removed by placing the crucible on a pipeclay triangle over a porcelain dish so that the bottom of the crucible is immersed in the given solvent. By gradually heating the solvent, not to boiling, the precipitate will soon dissolve. Care must be taken with carbonates, or effervescence may cause particles of the felt to be dislodged.[1]

A list of solvents for various precipitates, taken from Swett's paper, is given in the Appendix—Table XCIV., page 730.

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[1] Precipitates sometimes cling tenaciously to the surface of the platinum felt, and if they are removed mechanically, will often take particles of felt with them. In cases where it may be necessary to mechanically remove precipitate, a perforated disc of platinum of suitable size may be placed on top of the platinum felt, as recommended by Richards and Staehler (*l.c.*).

CHAPTER VI.

HEATING AND DRYING.

§ 55. Heating.

Bunsen's Burner.—The burner, fig. 136, devised by R. Bunsen about 1855[1] is the best type for general purposes. It is too well known to need any description.[2] There are a number of modifications. In Marshall's type of Bunsen's burner[3] the burner tube passes straight through the base, and the gas enters at the side. These are the so-called "drip-proof" burners, since there is no central gas jet to become choked with matter falling down the tube. The regulator works beneath the base. Teclu's burner[4] (figs. 109 and 145) is a useful modification of Bunsen's burner. It can give a rather higher temperature than the original form of Bunsen's burner. The gas and air can be regulated so as to give anything between a luminous smoky flame and a "blowpipe" flame. The latter will decompose calcium carbonate. Porcelain burners (figs. 100 and 160) are convenient for use in hoods, etc., where metal burners would be corroded by the fumes.

Accessories for Bunsen's Burners.—The burners may be provided with supports for holding the frustum of a copper cone to protect the flame from draughts (figs. 138 and 184); with Lendrich's[5] jets for splitting the flame into three, four (fig. 60), or five smaller flames. The multiple flame so obtained is better than the ordinary single flame for heating basins, beakers, etc., over wire gauze. For instance, there is less risk of spitting at the later stages of an evaporation;[6] with a mushroom top for spreading the flame (fig. 162); with a jet for giving a flat flame (fig. 113); an attachment for heating tubes, *e.g.*, Weston's jet (fig. 122) or Ramsay's jet (fig. 145); with a ring top[7] for heating a crucible from above downwards (fig. 170). Some burners are supplied with a rod permanently fixed to the base. The rod is intended to support a retort ring carrying a triangle, which can be adjusted at any height for heating crucibles, basins, etc.; or a similar support may be temporarily attached to the outside of the tube of the burner, as shown in fig. 60.[1] The burner may also be provided with two slots which fit a fork sliding up and down a retort stand. The burner can then be adjusted at any required height (figs. 125, 162). The burner may also have a by-pass for a "pilot" light (fig. 137). This is a convenience when a burner has to be frequently lighted and extinguished. There are several types of burner in which air and gas are simultaneously regulated so that, by merely turning a stopcock, the flame can be turned quite low without being extinguished, or "striking back." There is then no need for a pilot light—*e.g.*, Finkener's and Pethybridge's burners.[2] The burner can also be provided with a jacket to prevent losses by the radiation of heat—*e.g.*, fig. 109.

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[1] P. Desaga, *Dingler's Journ.*, **113**. 340, 1857. For the efficiency of Bunsen's burners, see H. O'Connor, *Chem. Trade Journ.*, **51**. 461, 1912.

[2] The burners are usually attached to the supply nozzle by means of rubber tubing. A drop of glycerol between the rubber and the metal will prevent the rubber sticking fast—A. H. Church, *Chem. News*, **35**. 1, 1877. Flexible copper tubing is ultimately cheaper and safer than rubber tubing. There is a variety of "flexible" copper tubing on the market which is a nuisance on the bench, since it is too rigid.

[3] H. Marshall, *Journ. Soc. Chem. Ind.*, **16**. 395, 1897; *Brit. Pat. No.* 238, 1897; W. P. Evans, *ib.*, **16**. 863, 1897; F. Allihn, *Chem. Ztg.*, **23**. 996, 1899.

[4] N. Teclu, *Zeit. anal. Chem.*, **31**. 429, 1892; **33**. 450, 1894; *Journ. prakt. Chem.* (2), **47**. 535, 1893.

[5] K. Lendrich, *Zeit. Nahr. Genuss.*, **12**. 593, 1906; *D.R.G.M.* 279398 to 279400, 1903.

[6] A. A. Blair (*The Chemical Analysis of Iron*, Philadelphia, 20, 1908) recommends placing a thin circular disc of asbestos paper, about 2 cm. diameter, on the wire gauze so as to cover the point of the Bunsen's flame, and throw the heat more to the sides of the dish being heated on the gauze.

[7] L. Hormuth, *Zeit. anal. Chem.*, **43**. 231, 1904.

Argand Burners.—The Bunsen's burner can be fitted with a ring for supporting a mica chimney. This is convenient for low-temperature ignitions. The flame is not affected by air-currents. This modification imitates the Argand burner, which is coming into general use for charring filter papers, low-temperature ignitions, etc., particularly where uniformity of temperature is desirable. The Argand burner is provided with a steatite jet, and with a metal or a mica chimney (fig. 112). The so-called "micro-burners" are useful sources of heat when a bath is to be heated to a low temperature for a long time, and when a comparatively low uniform temperature is desired. See fig. 198, page 635.

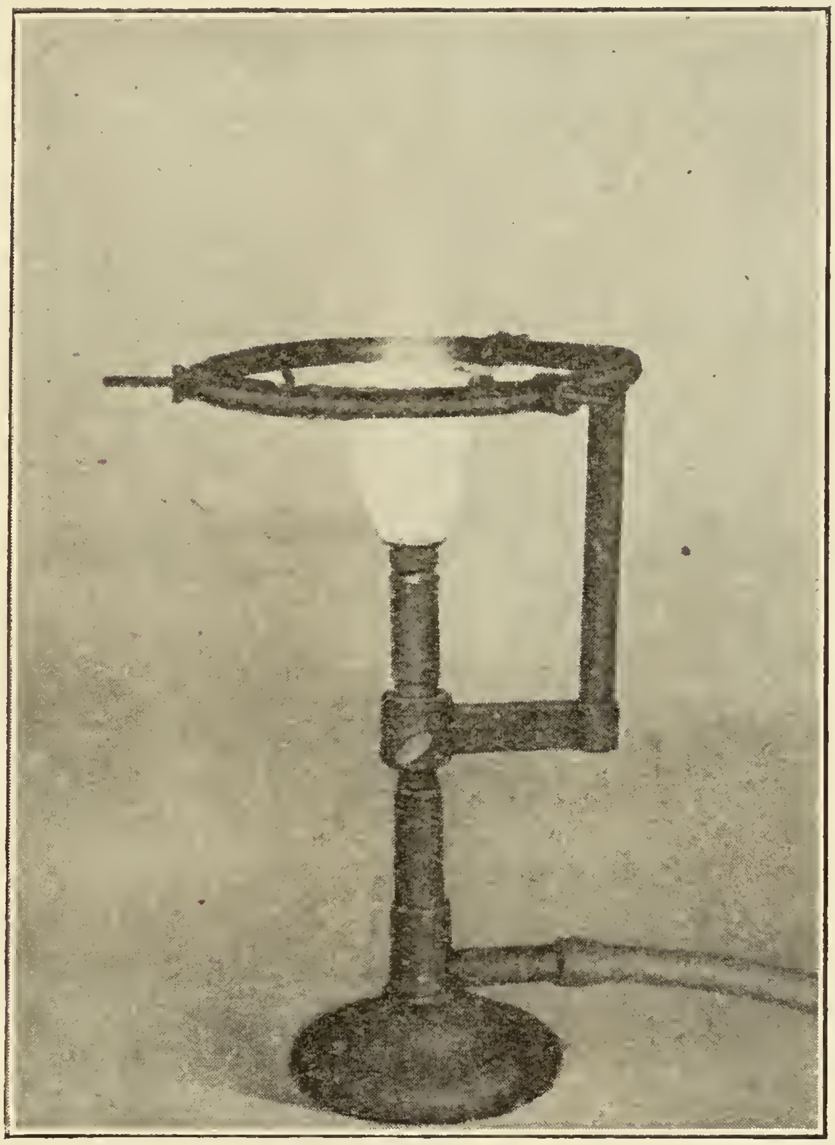

Fig. 60.—Stand for Bunsen's burner.

Méker's Burners.—G. Méker's burners (figs. 61 and 94)[3] are probably the best high-temperature burners on the market. Their virtues are usually extolled in the dealers' catalogues.[1] They can be obtained with or without a blast (figs. 61 and 92) attachment. The blast Méker's burner is quite satisfactory for silica and other ignitions requiring a blast.[2] Méker's burners are also adapted for heating muffles, and for crucible furnaces. There are many advantages in making ignitions in muffles when a large number have to be made. The muffle furnace shown in fig. 61 has a fireclay muffle, and is heated by a blast Méker's burner; quartz muffles are not suited for the blast furnaces.

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[1] See L. Quennessen, *Chem. News*, 88. 66, 1903.

[2] *Chem. Eng. Works Chem.*, 1. 187, 1911. For stands to enable crucible to be rotated while it is being heated, see Hodes and Göbel, *Chem. Ztg.*, 35. 488, 1911.

[3] G. Méker, *Chem. News*, 99. 88, 1909 ; C. G. Fischer, *Met. Chem. Eng.*, 9. 222, 1911.

Hot Plates.—Sand baths are convenient for heating round-bottomed vessels, but they are dirty at best, and they should be banished from analytical laboratories. Quartz plates or plates of asbestos millboard are frequently used, but the asbestos soon deteriorates where the flame strikes. Quartz plates are more economical, since they last a long time.[3] Plates of cast iron, or boiler plate,[4] about 0·5 cm. thick, resting on a tripod or quadripod, and heated by a ring or a Fletcher's burner, are preferable to the sand bath.[5]

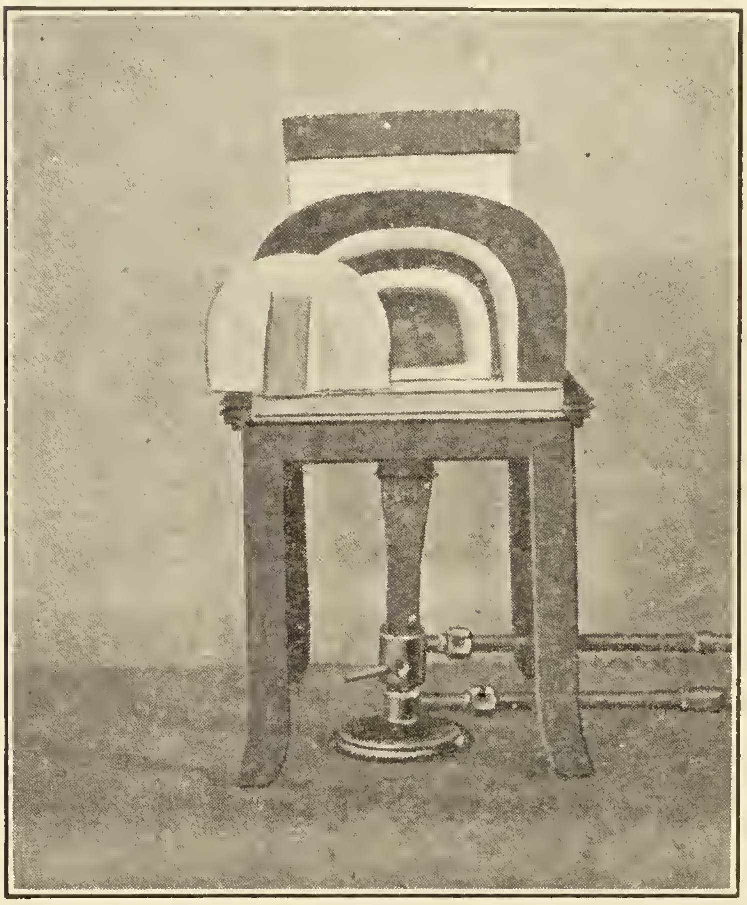

FIG. 61.—Blast Méker's burner with muffle.

Radiator.—When a liquid is to be evaporated or a moist solid is to be heated in a crucible, to avoid spattering, it is generally safer to heat the crucible in a so-called "radiator," rather than on a hot plate. The "radiator" corresponds with the "nickel beaker" of Jannasch.[6] The most convenient form of radiator is a nickel crucible with a triangle placed inside, so arranged that the crucible to be heated is approximately equidistant from the sides and bottom of the nickel crucible. The nickel crucible and contents are heated over a small flame, when the liquid in the inner crucible is soon evaporated. The lid can then be placed on the nickel crucible, and the contents of the inner crucible baked at a higher temperature. Several modifications naturally suggest themselves. The ring burner, fig. 96, page 170, serves a similar purpose.

Electric Heating.—If an electrical current is available, a great deal of the heating may be done more cheaply and cleanly than with gas. The gas supplied at the present day is very dirty. Baths and utensils soon become covered with thick crusts of naphthalene, etc., when heated by gas. Electricity is the ideal heating agent for a laboratory. Hot plates, air and water baths, hot-jacketed funnels, muffles, etc., can all be conveniently heated by this agent. With a little ingenuity, too, the cost of the necessary apparatus for electrical heating is less than for gas. Improvements are being published nearly every month, so that published descriptions of apparatus are soon obsolete.

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[1] But not exaggerated in, say, the catalogue of the Cambridge Scientific Instrument Co.

[2] The blast for the burner photographed in fig. 61 is supplied by a Root's blower. It gives excellent results. A double water-injector pump, fixed on to a water tap, was found quite satisfactory with a 13-cm. Méker's blast burner. This latter type of blower has the advantage that it can also be used for the exhaustion of filtration flasks, desiccators, etc. Certain types of crucible furnaces which will give the necessary temperature, are to be avoided because they dent the platinum crucible when it is heated while resting between the fireclay projections.

[3] E. Erlenmeyer, *Zeit. Chem. Pharm.*, **8**. 639, 1864; C. Weigelt, *Rep. anal. Chem.*, **1**. 9, 1881.

[4] Cast iron is less inclined to warp than wrought iron.

[5] Nickel wire gauze, it may be added, does not "rust or perish" to the extent that other gauzes do.—H. L. Robinson, *Chem. News*, **76**. 253, 1897.

[6] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 37, 1904; W. M. Thornton, *Journ. Ind. Eng. Chem.*, **3**. 418, 1911; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Berlin, 24, 1911; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 31, 1910.

Triangles.—Plain pipeclay, porcelain, or quartz triangles, fig. 62*a*, with iron, or, better, nickel or nichrome[1] wire are employed for general work. Quartz triangles are best for high-temperature work; they are far more durable than porcelain or pipeclay, and better resist sudden changes of temperature. Coleman[2] has suggested placing a projection in the middle of the pipeclay tubes as indicated in fig. 62*b*. These projections allow the flame to play about the crucible,[3] and less heat is thus lost by conduction; but they are liable to dent platinum crucibles. The same remark applies to Schmelck's triangles.[4] Many modifications have been suggested. Some types of triangle can be adjusted to fit crucibles of different sizes, but generally these triangles are something of a nuisance after they have been in use some time. The springs and screws get out of order.[5] Lienau's triangle, fig. 62*c*, is supposed to allow expansion without breaking the pipeclay.[6] Plain platinum triangles, fig. 62*d*, are generally used for platinum crucibles. They must be made of stout platinum wire, and this is costly. If a platinum crucible be blasted on a platinum triangle, the triangle may stick to the crucible. The two can only be separated by tearing a piece out of the crucible. Hence, use quartz triangles for platinum crucibles which are to be "blasted." Hebebrand[7] made triangles of nickel with platinum buttons at the points where the triangle would come in contact with the platinum crucible. The plain platinum triangle gives best results for general work, but Hebebrand's triangles work all right for low-temperature work. The triangle shown in fig. 60 can be screwed tight when the wires have begun to sag.

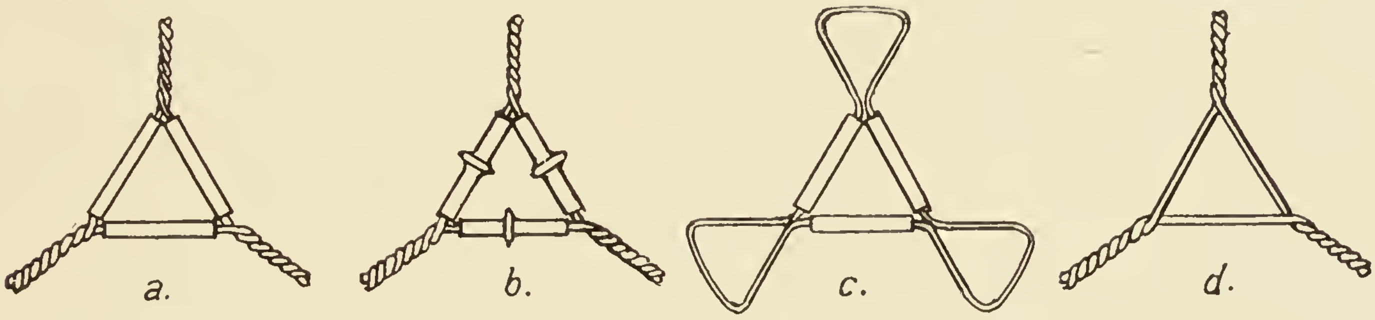

Fig. 62.—Triangles.

Hot platinum crucibles must not be lifted with iron, nickel, or brass tongs in such a way that these metals come in contact with the hot platinum. Brass tongs with a pair of platinum shoes (fig. 94) over the tips are generally used. Another form recommended by Blair[8] is illustrated by fig. 63. The body of the tongs is made of iron. The part *a* to *b* is of platinum, and fits over or into (fig. 63) the iron ends of the tongs. By means of these tongs the crucible can be clasped and held firmly without any danger of bending the crucible. These tongs are recommended for holding crucibles containing liquid fusions. In view of the high price of platinum, I prefer to cover the "bow" of a pair of ordinary brass tongs with platinum foil. This is cheaper and quite as effective. If the tongs be placed on the bench points downwards after holding a hot crucible, the hot points are liable to pick up matter from the bench, which is afterwards transferred to the crucible.

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[1] R. C. Benner (*Eng. Min. Journ.*, **91**. 360, 1911) prefers nichrome wire—that is, an alloy of chromium and nickel—since it does not oxidise so readily in the blast lamp.

[2] J. B. Coleman, *Journ. Soc. Chem. Ind.*, **11**. 326, 1892; C. Winkler, *Zeit. anal. Chem.*, **18**. 259, 1879; E. Murmann, *Oester. Chem. Ztg.*, **12**. 145, 1911.

[3] Von Heygendorff (*Chem. Ztg.*, **35**. 523, 1911) uses pipeclay beads instead of clay tubes.

[4] L. Schmelck, *Chem. Ztg.*, **20**. 407, 1895.

[5] L. Martius, *Chem. Ztg.*, **24**. 15, 1900; H. Lienau, *ib.*, **29**. 991, 1905.

[6] The triangle should be so placed on the tripod that it is least likely to let the crucible fall should the wires be burnt through during an ignition, and those triangles least likely to let the crucible fall under these conditions are generally best.

[7] A. Hebebrand, *Chem. Ztg.*, **24**. 37, 1900.

[8] A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 34, 1908.

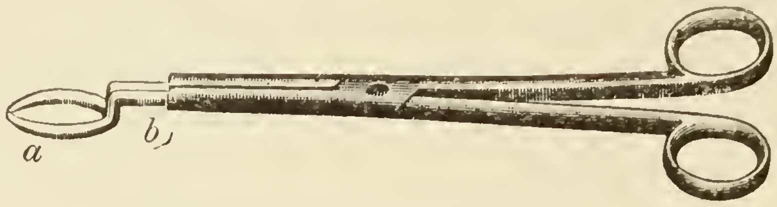

Fig. 63.—Platinum-tipped tongs.

§ 56. Platinum Apparatus.

Modern platinum ware is inferior in quality to that on the market some years ago, and the cause has been the subject of special inquiry by a committee of the American Chemical Society.[1] The main objections are: "(1) undue loss of weight on ignition; (2) undue loss in weight on acid treatment, especially after strong ignition; (3) unsightly appearance of the surface after strong ignition, especially after the initial stages of heating; (4) adhesion of crucibles and dishes to triangles sometimes to such an extent as to leave an indentation on the vessel at the points of contact with the triangle, even when complete cooling has been reached before the two are separated; (5) alkalinity of the surface of the ware after strong ignition; (6) blistering; and (7) development of cracks after continued heating." It is the general opinion that the trouble arises from the working of scrap platinum into chemical ware. The main difficulties here mentioned are not characteristic of platinum ware from some of the best manufacturers.

Many new and old platinum crucibles lose weight on long blasting. This is generally thought to be due to the distillation of iridium from the platinum alloy.[2] If a crucible suffers from this disease, the rate of loss per five minutes' blasting must be determined, and an allowance made. Beilstein[3] states that the loss in weight becomes less after repeated ignition. On the other hand, Hall[4] found the loss on the twentieth heating even greater than the first. The following numbers represent the loss in weight which a new platinum crucible suffered after half-hour ignitions on a blast. The weight of the new crucible was 22·5299 grms.:

0·0005; 0·0004; 0·0003; 0·0002; 0·0001 grm.

After a month's use, the crucible remained practically constant in weight during the same period of blasting.[1] Another crucible did not show this phenomenon, but seemed to steadily lose about 0·0003 grm. per half an hour's blasting. The only inference to be drawn from these discordant observations is that the alloys used for making different crucibles are not the same. With luck, crucibles can be obtained which undergo practically no loss when heated in the blast. Crucibles which suffer a change in the rate of loss with time must have the correction determined at frequent intervals. If a crucible loses 0·2 mgrm. on ten minutes' blasting, the necessary correction is obvious. It is sometimes convenient to take the weight of the crucible after the ignition.

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[1] "Preliminary Report of the Committee on the Quality of Platinum Utensils," *Journ. Ind. Eng. Chem.*, 3. 986, 1911.

[2] L. L. de Koninck, *Zeit. anal. Chem.*, **18**. 569, 1879. H. Kayser (*Wied. Ann.*, **34**. 607, 1888) noticed that platinum lost weight when heated in tubes in a current of air, and assumed that the platinum gave up fine particles to the air. L. Elsner (*Journ. prakt. Chem.* (1), **99**. 257, 1866) found platinum crucibles lost weight when heated in porcelain ovens. E. Sonstadt, *Chem. News*, **13**. 145, 1866; G. A. Hulett and H. W. Berger, *Journ. Amer. Chem. Soc.*, **26**. 1512, 1904; E. Goldstein, *Ber.*, **37**. 4147, 1904. G. C. Wittstein (*Dingler's Journ.*, **179**. 299, 1866) referred the loss to osmium, but F. Stolba (*ib.*, **198**. 177, 1870) pointed out that the loss of weight is greater than the amount of osmium in the platinum ore.

[3] F. Beilstein, *Pharm. Zeit. Russland*, **19**. 630, 1880.

[4] R. W. Hall, *Journ. Amer. Chem. Soc.*, **22**. 494, 1900.

Although platinum is not oxidised nor seriously attacked by the single acids used in analytical chemistry, many substances attack and combine with platinum at comparatively low temperatures.[2]

The more important precautions to be considered in using platinum vessels may be conveniently summarised in the following decalogue :—

1. Do not heat "unknown" substances in platinum vessels.

2. Always keep the platinum ware bright and clean. For this purpose use fine sea sand, with rounded grains and free from grit, as a polishing powder.[3] This removes most impurities, and polishes without serious loss. Apply the sand with the finger. Gmelin's recommendation to fuse a little potassium bisulphate in the dish is a good method for cleaning the inside of badly tarnished crucibles.[4] The bisulphate is poured out of the crucible while fluid, and the crucible then cleaned with water and sand.

3. Never heat the platinum crucible or dish in contact with iron or metals other than platinum; nor let hot platinum be placed in contact with foreign metals. Use nothing but pipeclay, quartz, or platinum triangles, and platinum-shod tongs.[5]

4. Do not fuse metals in a platinum crucible, nor heat in the crucible salts of the easily reducible metals, particularly salts of lead,[6] silver, arsenic, antimony, copper, bismuth, tin, etc. See page 266.

5. Do not heat phosphides nor the sulphides of the metals in platinum crucibles. Sulphur alone has no action.[7] Phosphorus attacks platinum.

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[1] The lid of this crucible contained about 1·5 per cent. of iridium.

[2] For the corrosion of platinum by ammonium and potassium bromoplatinates, see G. Méker, *Compt. Rend.*, **125**. 1029, 1897 ; *Chem. News*, **77**. 19, 1898 ; by potassium bisulphate, see page 186 ; by borax and boric acid ; by ferric chloride ($4FeCl_3 + Pt = PtCl_4 + 4FeCl_2$), see A. Béchamp and C. Saint Pierre, *Compt. Rend.*, *Chem. News*, **4**. 284, 1861 ; by ignition of ammonium chloroplatinate, see F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 225, 1910 ; by solutions of titanic hydroxide in the presence of nitric or sulphuric acid, see H. Rose, *Traité Complet de Chimie Analytique*, Paris, **1**. 1028, 1859 ; W. B. Giles, *Chem. News*, **99**. 4, 1909 ; by sulphuric acid (A. Scheurer-Kestner, *Compt. Rend.*, **91**. 59, 1880 ; **86**. 1082, 1878 ; *Bull. Soc. Chim.* (2), **24**. 501, 1875 ; (2), **30**. 28, 1898 ; M. Delépine, *Compt. Rend.*, **141**. 886, 1013, 1905 ; *Chem. News*, **93**. 108, 120, 1906 ; L. Quennessen, *ib.*, **93**. 271, 1906 ; J. T. Conroy, *Journ. Soc. Chem. Ind.*, **22**. 465, 1903 ; L. R. W. M'Cay, *Inter. Cong. App. Chem.*, **8**. 351, 1912) ; by sodium carbonate, see page 163 ; and by selenium compounds, page 441.

[3] F. Stolba (*Dingler's Journ.*, **198**. 178, 1870) says good sand for the purpose may be obtained by shaking dried sponges.

[4] If outside, put the bisulphate in a dish of suitable size, and allow the flux to completely envelop the vessel to be cleaned. F. Winkle (*Chem. Ztg.*, **23**. 803, 1899) recommends borax instead of potassium bisulphate for crucibles stained by the ignition of plant ashes. F. Stolba (*Dingler's Journ.*, **221**. 135, 1877) cleans dirty crucibles by melting equal parts of boron fluoride and boric acid in the crucible.

[5] Sodium amalgam is useful for cleaning platinum stained with foreign metals (*Chem. News*, **2**. 286, 1860). The amalgam is gently rubbed on the platinum with a cloth, and then moistened with water. This oxidises the sodium, and leaves the mercury free to amalgamate with the foreign metals. The mercury is wiped off, and the crucible cleaned with sand.

[6] Unfortunately, we sometimes have to take risks ; but never if it can be avoided.

[7] W. C. Heraeus and W. Geibel, *Zeit. angew. Chem.*, **20**. 1892, 1907.

Phosphates, under reducing conditions,[1] may form phosphides and phosphorus, which attack the metal.

6. Alkaline carbonates do not attack platinum very much, but the attack by caustic alkalies and alkaline earths is serious—particularly lithium and barium oxides. Hence, alkaline nitrates, nitrites, hydroxides, and cyanides should not be heated in contact with platinum, if it can be avoided.

7. Do not use aqua regia or free chlorine in contact with platinum. Watch for reactions (*e.g.* nitrates, chlorides, etc.) in which chlorine might be liberated. For instance, hydrochloric acid and oxidising agents. A moment of thoughtlessness may render it necessary to purchase a new crucible.[2]

8. Direct contact of platinum with burning charcoal, coal, or coke must be avoided. The platinum becomes brittle and liable to fracture if this precaution be neglected.[3]

9. Never permit a smoky flame to be used in contact with platinum, since a grey film[4] is formed on the platinum in mild cases, and the platinum is quite disintegrated in bad cases. For a similar reason, do not let the inner cone of a Bunsen's flame come in contact with the metal.[5]

10. Platinum is easily bent,[6] and care must be taken not to bend the crucible in handling, gripping with the tongs, etc.[7]

§ 57. Desiccators.

Fig. 64 represents convenient desiccators. That illustrated in fig. 64A is intended for general use—the so-called Scheibler's desiccator. The desiccating agent is placed in the bottom of the desiccator; a porcelain plate, with suitable holes, serves as a support for the crucibles and dishes. An aluminium plate is sometimes preferred, because it cools the crucibles, etc., rather more rapidly than porcelain. The crucible support rests on a ledge formed by a constriction in the walls of the desiccator. If the substance is to be dried *in vacuo*, the form fig. 64B can be used. This resembles fig. 64A, but it has a glass stopcock fixed in the lid. The desiccator can thus be connected with an air-pump. To open an exhausted desiccator, turn the stopcock very slowly, or a current of air may displace the powder under investigation. The rim of the desiccator which comes in contact with the lid, as well as the stopcock, should be smeared with vaseline, or, better, with a mixture of vaseline and beeswax melted together.

There is a fault with these desiccators. Moist air is lighter than dry air. Hence, it is bad on principle to place the desiccating agent at the bottom of the desiccator, beneath the substance to be dried. The action is then dependent upon the slow diffusion of the lighter moist air downwards. Hempel[1] devised a desiccator in which the drying agent is placed above the substance to be dried. The action is said to be more rapid because of the circulation induced by the natural tendency of the light moist air to accumulate in the upper part of the desiccator.[2] This argument does not apply to drying *in vacuo*, though it appears a valid objection to the form shown in fig. 64A. Fig. 64C represents Hempel's improved desiccator. The main objection to this type is that the acid is apt to spill, particularly when the desiccator is being opened.

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[1] S. Kern (*Chem. News*, **35.** 77, 1877) refers to the attack of platinum by the sulphur and carbon compounds in coal-gas.

[2] Old crucibles are purchased by dealers in "scrap" platinum.

[3] P. Schützenberger and A. Colson, *Compt. Rend.*, **94.** 26, 1882; A. Colson, *ib.* **94.** 1710, 1882; **82.** 591, 1876; J. Boussingault, *Ann. Chim. Phys.* (2), **16.** 5, 1821; C. L. Berthollet, *ib.* (1) **67.** 88, 1808; C. G. Memminger, *Amer. Chem. Journ.*, **7.** 172, 1886. V. Meyer, *Chem. News*, **73.** 235, 1896; A. B. Griffiths (*Chem. News*, **51.** 97, 1885) says "platinum fuses at a comparatively low temparature when heated in contact with carbon."

[4] Another type of grey film is formed even when the platinum is only heated in an oxidising flame. O. L. Erdmann (*Journ. prakt. Chem.* (1), **79.** 117, 1860; *Chem. News*, **2.** 256, 1860) showed that this film is due to a surface molecular change (crystallisation—W. Rosenhain, *Proc. Roy. Soc.*, **70.** 252, 1902), and is not attended by a gain or loss of weight. The stain should always be scoured off as soon as it is formed, otherwise the devitrification is inclined to spread.

[5] A. Rémont, *Bull. Soc. Chim.* (2), **35.** 486, 1881. H. Petrzilka (*Zeit. angew. Chem.*, **7.** 255, 1894) recommended a gilded platinum protective capsule to resist attack by smoky flames.

[6] A. A. Blair (*The Chemical Analysis of Iron*, Philadelphia, 33, 1908) recommends the use of a wooden plug the same shape as the inside of the crucible, to be used for straightening the crucible when it is bent.

[7] For soldering and repairing crucibles, see J. W. Pratt, *Chem. News*, **51.** 181, 1885; H. J. Seaman, *ib.*, **49.** 274, 1884; T. Garside, *ib.*, **38.** 65, 1878.

When the loss on ignition of certain clays is to be determined, and the clays, after ignition, are cooled in the usual manner, it is very difficult to get constant results. This is particularly noticeable when the blast is not very powerful.

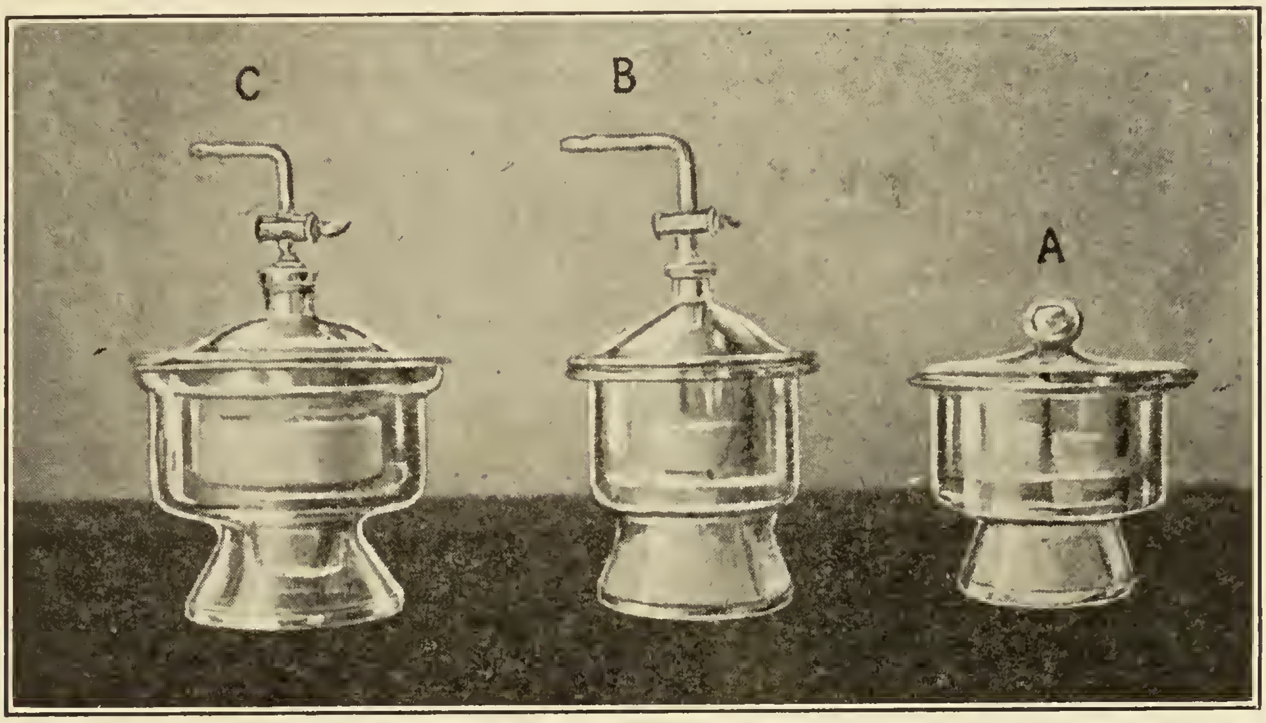

Fig. 64.—Desiccators.

The difficulty is eliminated if the ignited clay be cooled *in vacuo*. The trouble arises from the fact that clays, dehydrated at a comparatively low temperature, absorb the dry gases in an ordinary desiccator in a remarkable manner. As much as 1·5 per cent. may be so absorbed.[3]

Granulated calcium chloride, concentrated sulphuric acid, and phosphorus pentoxide are employed as desiccating agents. The drying agents require attention. The sulphuric acid should be frequently renewed, since that which has stood a long time in a desiccator is ineffective;[4] and, if it has become discoloured, owing to contamination with dust, etc., sulphur dioxide may be given off (page 7), and this can sometimes be detected by its odour. Pumice soaked in concentrated sulphuric acid is excellent. Phosphorus pentoxide soon becomes ineffective owing to the glazing of the surface with metaphosphoric acid, and hence this agent is not used except under special circumstances. Fresh granulated calcium chloride is most useful for general work. Kral[1] prefers a mixture of calcium chloride and quicklime in place of calcium chloride alone.[2]

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[1] W. Hempel, *Ber.*, **23**. 3566, 1890 ; *Zeit. angew. Chem.*, **4**. 84, 200, 1891 ; F. Cochius, *Chem. Ztg.*, **24**. 266, 1900 ; E. Biltz, *Pharm. Centrb.*, **12**. 353, 453, 1890. For the "ether" vacuum desiccator, F. G. Benedict and C. R. Manning, *Amer. Chem. Journ.*, **27**. 340, 1902 ; H. C. Gore, *Journ. Amer. Chem. Soc.*, **28**. 835, 1906 ; E. Donzard, *Amer. Journ. Pharm.*, **80**. 588, 1908.

[2] There is also the objection that the air in the interior expands when a hot crucible is introduced. On cooling, a partial vacuum may be produced, which renders the removal of the lid difficult. Hence, some prefer a desiccator with a side tubulure in which is fitted a calcium chloride tube which provides for the free circulation of dry air.—A. R. Leeds, *Chem. News*, **23**. 177, 1871.

[3] C. Friedel, *Compt. Rend.*, **122**. 1006, 1896 ; *Bull. Soc. Min.*, **19**. 14, 94, 1896 ; **22**. 5, 84, 1899 ; J. W. Mellor and A. D. Holdcroft. *Trans. Eng. Cer. Soc.*, **10**. 94, 1911.

[4] W. F. Hillebrand, *Amer. Chem. Journ.* **14**. 6, 1892.

§ 58. Laboratory Hoods, Fume Chambers.

In quantitative analysis, where a great many evaporations are conducted on a water bath, it is necessary to protect the liquids from dust during the evaporation. The arrangement shown in fig. 95, page 168, is convenient for single evaporations,[3] but where many evaporations have to be made, special closets are advisable. In silicate analyses, great volumes of hydrochloric acid, steam, and ammoniacal vapours are delivered into the atmosphere of the laboratory by evaporating liquids, and these vapours condense on the metal work; this sets up rapid and serious corrosion. Hence, an efficient fume closet is necessary for accurate work, for protecting the health of the worker, and for the preservation of apparatus in the laboratory. The comfort of the laboratory is largely determined by the efficiency of the hood.

The fume chamber must have an efficient draught independent of atmospheric conditions; and it must protect the exposed surface of evaporating liquids from dust.

The need for a vigorous draught is most emphasised in dealing with operations in which hydrofluoric acid vapours, hydrogen sulphide, and other noxious vapours are evolved; while the need for protection from dust is most pronounced when liquids are evaporating in shallow basins. If a large volume of air be passing through the hood, the risk of contamination from dust may be greater than when the draught is less. Hence, it may be advisable to install two types of hood: one specially designed for vigorous draught, and the other specially designed to prevent contamination from falling dust.

In the former type of hood—the fume closet—the chamber should be relatively small. A number of small hoods are more efficient than one large hood. The carrying capacity of the air for moisture, and the draught of the hood, are largely dependent upon the slight heating which the air receives in the chamber. In a large hood the warmed air is chilled and its carrying capacity for moisture, etc., is reduced, so that the fumes are not carried through the outlet provided, but work their way into the laboratory. The upper roof of the chamber should not taper too abruptly, and, if possible, the exit flue should be vertical throughout its entire length, so that the rising air may be baffled as little as possible. The sectional area of the exit flue should be about one-third the floor area. Thus, in a chamber with a floor $3 \times 1\frac{1}{2}$ sq. ft. the vertical flue should be about 4×4 sq. ins. For structural reasons it is not always convenient to provide a vertical flue. When the exit leads into a

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[1] H. Kral (*Pharm. Centr.*, **37.** 105, 1895) also recommends fused potassium bisulphate in place of sulphuric acid. The "spent" bisulphate can be regenerated by fusion.

[2] For the amount of moisture left in gases by desiccating agents—sulphuric acid, zinc and calcium bromides and chlorides, phosphorus pentoxide, and anhydrous copper sulphate, see R. Fresenius, *Zeit. anal. Chem.*, **4.** 177, 1865; C. Voit, *ib.*, **15.** 432, 1876; H. C. Dibbits, *ib.*, **15.** 121, 1876; P. A. Favre, *Ann. Chim. Phys.*, (3), **12.** 223, 1844; V. Regnault, *ib.* (3), **15.** 129, 1845; J. D. van der Plaats, *Rec. Trav. Chim.*, **6.** 45, 1889; E. G. Morley, *Amer. J. Science* (3), **30.** 140, 1885; (3), **34.** 199, 1887; *Journ. Amer. Chem. Soc.*, **26.** 1171, 1904; G. P. Baxter and R. D. Warren, *ib.*, **33.** 340, 1911. From this work it appears that the weight of residual water (in grams) left in a litre of gas dried by these different agents is:

Calcium chloride	0·0021	Calcium bromide	0·0002
Zinc bromide	0·0011	Sulphuric acid (1·838)	0·0000025
Zinc chloride	0 0008	Phosphorus pentoxide	0·000000025

For alumina as a desiccating agent, see F. M. G. Johnson, *Journ. Amer. Chem. Soc.*, **34.** 911, 1912.

[3] C. Winkler, *Ber.*, **21.** 3563, 1888; W. Hempel, *ib.*, **18.** 1434, 1885; C. M. Stewart, *Chem. News*, **52.** 208, 1885; C. R. McCabe, *Chem. Eng.*, **12.** 182, 1910; Spectator, *Chem. Ztg.*, **35.** 254, 1911.

chimney, the hood usually draws well, but if the exit flue in the ground floor of a building be led through the outer wall, the hood may be quite useless against the "back draught" set up by an unfavourable wind. A fan is then a valuable auxiliary, since it makes the action of the hood independent of the weather. Sometimes a jet of compressed air blown into the hood just below the base and directed into the exit flue, on the principle of a steam ejector, is very efficient, and there is then very little trouble with corrosion, as is the case when a fan is used. A gas burner placed just below the base of the exit flue will sometimes provide sufficient draught. The hood illustrated in fig. 65 is typical of a good fume closet.

For evaporating chambers a particularly vigorous draught is not needed, because the passage of a large volume of air over the surface of an evaporating liquid may lead to the deposition of dust from the air on to the liquid. If there is too little draught, the crystallising salts may "creep" badly, and the vapours will work back into the laboratory. There is also a risk of contamination from dirt falling down the exit flue, particularly on windy days. Hence, the exit flue of an evaporating chamber should not lead directly into a chimney.[1] Fresenius recommends leading the exit flue into a separate Russian chimney. "No fire must ever be made under this chimney, but it is most desirable to have this chimney placed close to another chimney kept constantly warm." Treadwell recommends the arrangement illustrated in fig. 66, where a kind of "dust trap" prevents the passage of dust into the evaporating chamber when a "back draught" occurs on a windy day. The hood has a glass roof A, and about 15 cm. below is a second glass plate B, which comes within 3 cm. of the inner wall of the hood throughout its whole length. Between the two glass plates is a clay pipe C, 15 cm. long and 5 cm. diameter, placed above the inner edge of the lower glass plate, and leading into the chimney in which a small gas flame D is burning. Dust, sand, etc., from the chimney "falls upon the plate B; none gets into the hood."

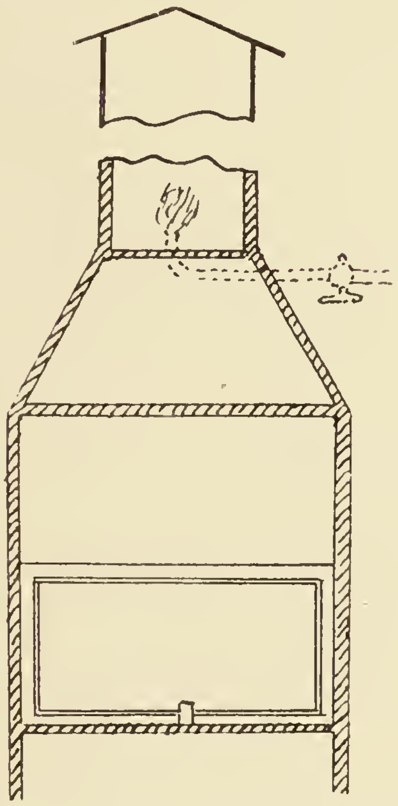

Fig. 65.—Front of fume chamber.

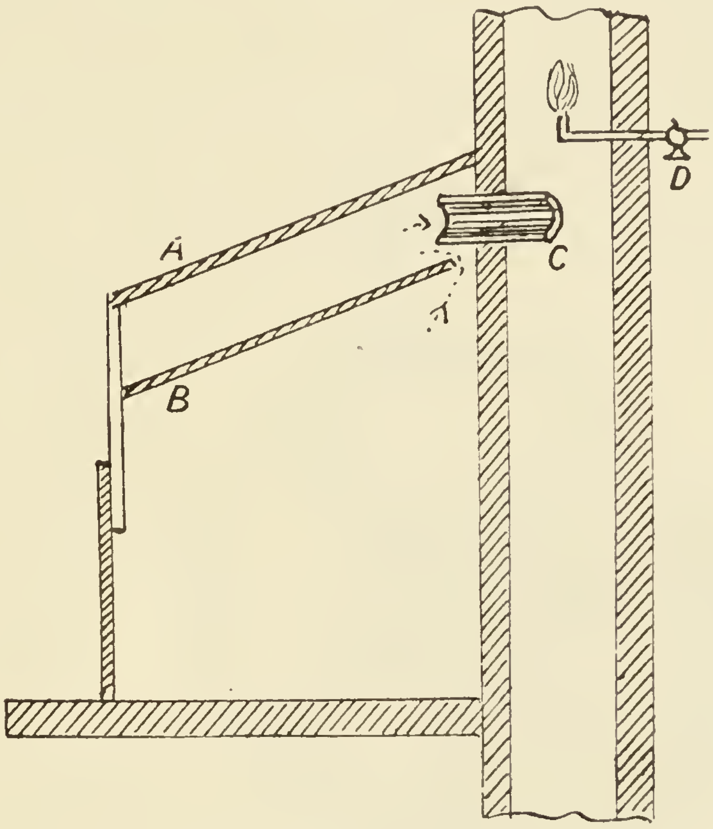

Fig. 66.—Treadwell's flue.

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[1] R. Fresenius, *Quantitative Chemical Analysis*, London, **1**. 62, 1876 ; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 26, 1911 ; H. S. Sherman, *Chem. Eng.*, **11**. 21, 1910 ; E. Keller, *Journ. Ind. Eng. Chem.*, **3**. 246, 1910 ; C. R. McCabe, *ib.*, **12**. 183, 1910 ; C. F. Mabery, *Journ. Anal. App. Chem.*, **6**. 247, 1892 ; J. K. Meade, *The Design and Equipment of Small Chemical Laboratories*, Chicago, 1908 ; T. H. Russell, *The Planning and Fitting-up of Chemical and Physical Laboratories*, London, 41, 1903. For contamination by paint from inside of hood, see A. Schaeffer, *Zeit. Nahr. Genuss.*, **24**. 403, 1912.

CHAPTER VII.

PULVERISATION AND GRINDING.

§ 59. Pulverising Large Quantities.

There is no difficulty in reducing friable materials to powder in, say, porcelain mortars, etc., but harder substances present some difficulty. It is almost impossible to pulverise hard, tough substances without some contamination from the crushing or grinding apparatus. For sampling, and for other experimental purposes, the breaking of stone, in bulk, down to particles, say 10's lawn, is commonly done in a crusher. Braun's jaw crusher[1]—fig. 67—is useful for crushing a large quantity of material. This machine reduces the material between a pair of jaws, one of which is stationary, and the other vibratory. The fineness of the grinding is regulated by opening or closing the jaws by a regulating screw. The jaws can be adjusted to crush material from a diameter of $2\frac{1}{2}$ in. to that which will pass a 10's lawn. For fine crushing, however, the material is best run, at least, through twice—once with the jaws comparatively wide apart; the second time with the jaws close together. The machine is run at about 200 revolutions per minute. It can be operated by power or hand. It should be perfectly clean before it is used.

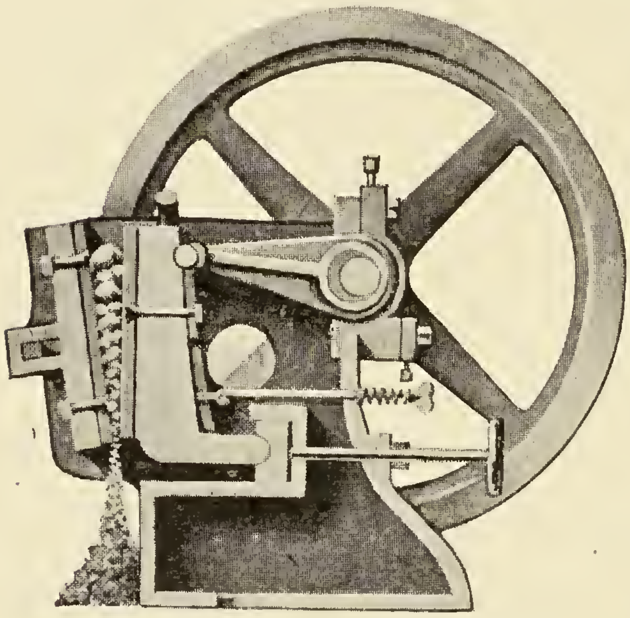

Fig. 67.—Braun's jaw crusher.

In Braun's disc pulveriser the material is pulverised between a pair of iron discs. A small machine will reduce 80 to 90 lbs. of material from $\frac{1}{4}$ in. mesh to 10's lawn per hour. It may be run by power or hand. There is always a tendency to contamination from the iron disc of the pulveriser or the steel jaws of the crusher. Hence the sample for analysis should be very carefully magneted if it has been passed through the jaw or disc crushers. The worn parts of either of the above machines are made interchangeable, and consequently repairs are easy.

§ 60. Pulverising Small Quantities.

Large lumps may be broken into coarse powder[2] by wrapping a lump in several folds of writing paper and striking it sharply with a hammer while it is resting on a steel plate placed upon a firm, solid support. The coarse fragments so obtained can be still further reduced on a hard steel plate (*a*, fig. 68) on which is placed a steel cylindrical ring *b*. A hard steel pestle *c* fits into the ring. The steel pestle and plate are made from the hardest "diamond" steel—hence the term "diamond mortar."[1] The fragment of rock to be pulverised is placed on the steel plate within the ring. The plate is placed on a firm support. The pestle is depressed by a few sharp blows with a mallet. Care must be taken not to grind or rub the metals against the fragments, otherwise the risk of contamination is greater. This is the case, for example, with the mortar of the type shown in fig. 69, which is made from the very best hardened tool steel, and is useful for breaking hard rocks. Most materials can be magneted after crushing so as to remove steel particles introduced during crushing.

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[1] F. W. Braun, *U.S. Pat. No.* 497802, 1902 ; K. Zulkowsky, *Zeit. anal. Chem* , 27. 24, 1888.

[2] If there are no objections, many minerals (felspar, flint, etc.), difficult to pulverise, become quite brittle if calcined and suddenly quenched in cold water

The magneting of a ground powder to remove fragments of iron from the crusher is conveniently done by means of an electro-magnet. A certain amount of discretion is needed, because, not only is iron derived from the crushing apparatus withdrawn, but certain magnetic minerals—magnetite, for example—may be removed at the same time. With the more powerful electro-magnets, minerals which are sometimes considered to be non-magnetic[2]—limonite, hematite, chromite, iron and copper pyrites, etc.—may be removed. This occurs with the more powerful electro-magnets which have their poles tapering to blunt points, and with the points close together. Hence, false results would be obtained in the analysis of certain materials if the powdered sample were first magneted by such instruments.

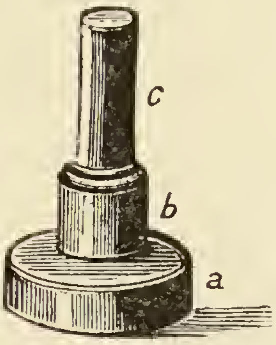

FIG. 68.—Abich's mortar and pestle.

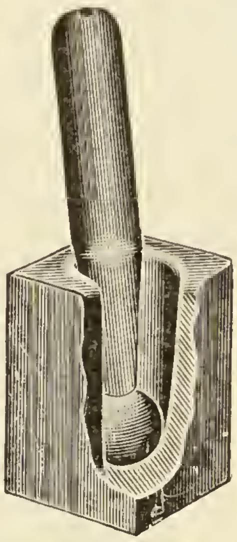

FIG. 69.—Steel mortar and pestle.

When the substance under investigation itself contains magnetic materials—magnetic oxide of iron, etc.—the magneting is not admissible, even though it is practically impossible to crush large or small quantities of hard material in iron vessels without contamination of iron. Hence the iron determination must necessarily be high.

The material should be crushed fine enough to allow it to be ground in an agate mortar without the particles flying off during grinding. Care must also be taken to grind all the sample in this way, otherwise the harder fragments may be unconsciously rejected and the softer particles alone retained for examination.[3]

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[1] Also called Abich's steel mortar, although it was not devised by H. Abich (*Pogg. Ann.*, 23. 309, 1831).

[2] But which are in reality feebly magnetic—M. Faraday, *Phil. Trans.*, 153. 1, 43, 1846; C. G. Gunther, *Electro-magnetic Ore Separation*, New York, 1909.

[3] For errors in the analysis of iron pyrites due to grinding with Wedgwood-ware mortars and pestles, see N. Glendinning and A. J. M. Edgar, *Chem. News*, 27. 1873.

§ 61. Grinding in Agate Mortars.

An agate mortar and pestle are usually employed for fine grinding. The mortar and pestle should be selected with care. They should be free from cracks and indentations. It is always necessary to be on guard against contamination from the grinding apparatus. Cracks and soft seams in an agate pestle and mortar are a source of danger. The small agate mortars and pestles are usually too short to hold with comfort. They should be fitted in wooden handles (fig. 70). Beginners most frequently err in charging the mortar with too much material. It is best to grind the material in small portions at a time until sufficient is obtained for the analysis.

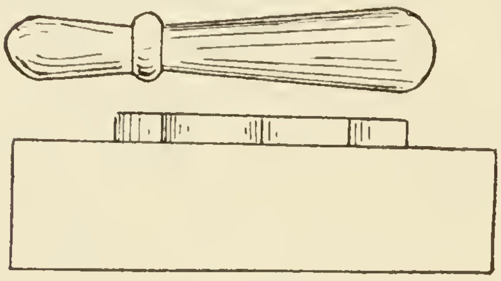
Fig. 70.—Agate pestle and mortar.

When large quantities of material have to be ground, an agate mortar and pestle driven by power can be used. Carling's instrument is superior to M'Kenna's.[1] These machines work automatically and with but little attention. The motions of the agate pestle and mortar simulate hand-grinding. In Carling's instrument, fig. 71, the table holding the mortar is rotated by a worm-and-worm wheel in the pedestal. This is driven by a chain band in the base. The pestle is worked by an eccentric movement on the rotating mortar. The machine is easily cleaned. To remove the mortar, depress the feeder lever, raise the pestle clear by pushing the spindle through its bearing, and loosen the

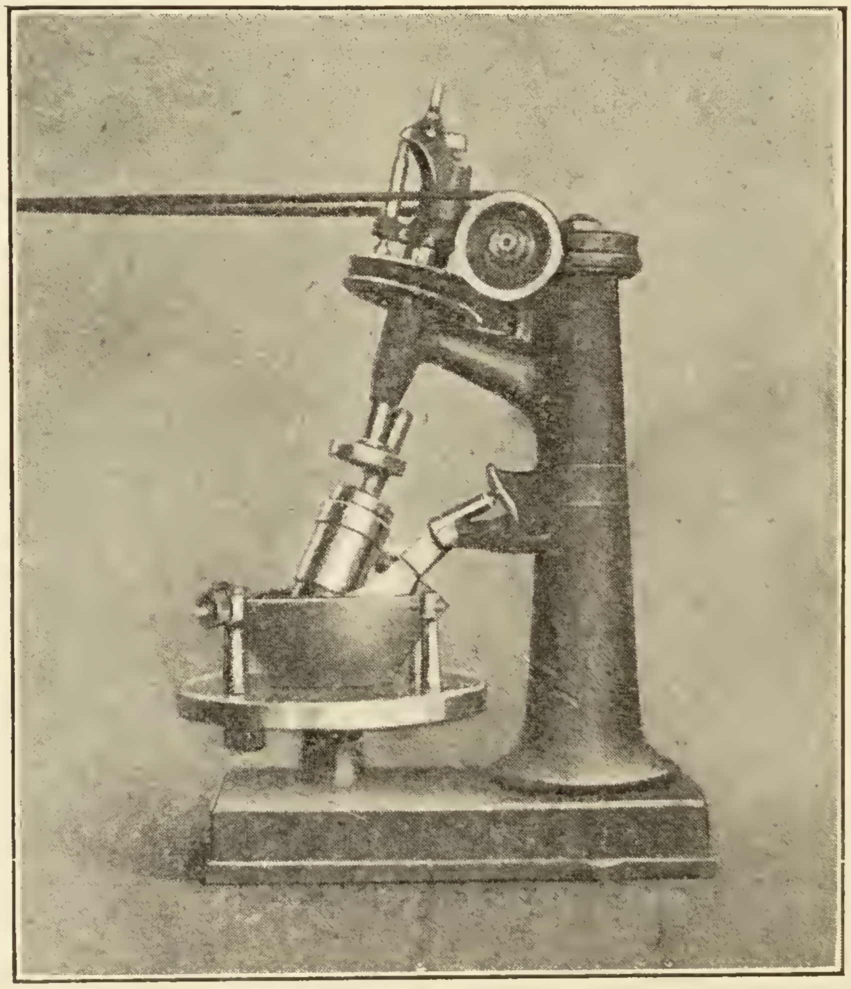
Fig. 71.—Carling's power-driven agate pestle and mortar.

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[1] K. Zulkowsky, *Ber.*, **20**. 2664, 1887 ; C. T. M'Kenna, *Eng. Min. Journ.*, **70**. 462, 1900 ; *Iron Age*, **66**. 9, 1900 ; W. H. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 55, 1910 ; J. W. Mellor, *Trans. Eng. Cer. Soc.*, **10**. 94, 1911.

knurled brass screws, one of which is attached to a loose pillar which, on being withdrawn, allows the mortar to be removed. The driving wheel should run from 100 to 150 revolutions per minute.

As a rule, a power-driven agate mortar and pestle wears more rapidly than one used for hand-grinding. The speed must not be great enough to project the powder over the sides of the mortar. The materials in the mortar must be protected from contamination by oil, etc., from the wheels and gearing. A copper cup may be attached to the handle of the pestle, and a rubber sheet wrapped round the axle to reduce the risk of contamination from oil, etc., on axles and wheels above the mortar. The machine can also be advantageously run in a glass case to protect the contents of the mortar from dust.

§ 62. The Dangers of Fine Grinding.

There are a few risks incidental to the operation of grinding which must be noticed. Fine grinding is not to be applied indiscriminately. It must not be assumed that the powders ground specially fine for the Smith's process for alkalies, for the determination of ferrous iron, for carbonate fusions, etc., have the same properties as coarse powders. The more important effects of fine grinding on the composition of a powder are as follows :—

1. *Contamination from the Grinding Apparatus.*—The finer the grinding the greater the risk of contamination from the grinding vessels, and, in consequence, the greater the variation in the amount of silica, etc., derived from the pestle and mortar.

Hempel[1] has investigated the effect of grinding 10 grms. of glass in mortars and pestles made of agate, steel, and cast iron until the glass passed through a given sieve. The results are given in Table XVII.

Table XVII.—Influence of Grinding Apparatus on the Composition of a Powder.

Material.	Mortar (Reibschale).		Pestle.	
	Weight.	Loss in weight.	Weight.	Loss in weight.
Agate	371·741	0·041	44·242	0·011
Steel (new)	295·078	0·029	134·647	0·0021
Steel (old)	295·049	0·005	134·645	0·0004
Cast iron (new)	884·917	0·041	144·383	0·0009
Cast iron (old)	884·825	0·014	144·382	0·0000
Green bottle glass	195·584	0·027	...	...

This table shows that the loss in weight, and consequently also the contamination of the materials being ground, is greater with agate mortars and pestles. Hempel supposes that steel mortars and pestles are the best for grinding purposes ; there is then less contamination. The *nature* of the contamination, however, presents a difficulty. Iron is one of the important impurities in clays, etc., and the analytical numbers for this impurity would be too uncertain if iron mortars and pestles were used for the grinding. The effect of the impurity derived from the agate has an inappreciable effect on the analytical numbers. It is therefore best to avoid, as much as possible, the use of the metal mortars and pestles, and keep to agate.[1]

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[1] W. Hempel, *Zeit. angew. Chem.*, 14. 843, 1901 ; G. A. James, *Chem. Eng.*, 14. 380, 1911 ; V. Lenher, *Journ. Ind. Eng. Chem.*, 4. 471, 1912.

2. *Gain and Loss of Hygroscopic Moisture.*—The fact that powders in "a very fine state of subdivision greedily absorb moisture from the air during the operation of weighing"[2] is well known. The speed of absorption is greater the finer the grinding. Thus, Day and Allan[3] have shown that coarsely ground felspar, containing little or no hygroscopic moisture, takes up progressively increasing amounts of moisture as the powder becomes finer, and the quantity so taken up may amount to 1 per cent. of the weight of the sample. Again, Hillebrand[4] found for a noritic rock the results indicated in Table XVIII.

Table XVIII.—Influence of Fineness of a Powder on Hygroscopicity.

Condition of rock.	Water.	
	Below 100°.	Over 100°.
60 apertures per cm. . . .	0·03	0·66
After 30 min. grinding . .	0·10	0·66
After 120 min. grinding . .	0·74	1·00

This all agrees with an old observation of Descharmes,[5] who showed that rock crystal (quartz) increased in weight on pulverisation to such an extent that the original weight might be doubled. Furthermore, Thugutt[6] has shown that some minerals take up water during fine grinding, while others—*e.g.* apophyllite—lose water. Hence, he infers that the hygroscopic moisture is best determined on a coarsely ground sample.

3. *Gain or Loss of Combined Water, Water of Crystallisation, etc.*—Bleeker[7] has noticed that in grinding crystallised magnesium sulphate 2·55 per cent. of water was lost during two hours' grinding with a Wedgwood-ware pestle and mortar; disodium hydrogen phosphate lost 1·85 per cent.; potash alum, 0·49 per cent. With barium chloride there was an increase of 2·11 per cent. in weight. Steiger obtained similar results with calcium sulphate.

4. *Oxidation of Ferrous Compounds.*—Mauzelius[8] has shown that with minerals containing ferrous compounds quite an appreciable amount is oxidised to ferric oxide during fine grinding. Thus, 5·13 per cent. of ferrous oxide was obtained on a coarsely ground sample, and 3·13 per cent. on the same sample finely ground. It is therefore obvious that the powder must be ground as coarsely as possible—say 120's to 150's lawn—when the ferrous oxide is to be

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[1] H. Wurtz (*Amer. J. Science* (2), **26**. 190, 1858) suggested removing the iron by digesting the powder with iodine water.

[2] R. W. Atkinson, *Chem. News*, **49**. 217, 1884.

[3] A. L. Day and E. T. Allen, *Amer. J. Science* (4), **19**. 93, 1909.

[4] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **30**. 1120, 1908.

[5] P. Descharmes, *Recueil Industriel*, **1**. 64, 1828.

[6] S. J. Thugutt, *Centr. Min.*, 677, 1909; F. von Kobell, *Journ. prakt. Chem.* (1), **107**. 150, 1869.

[7] J. B. Bleeker, *Chem. News*, **101**. 30, 1910; C. E. Gillette, *ib.*, **104**. 313, 1911.

[8] R. Mauzelius, *Sveriges Geol. Und. Arsbok*, **3**. 1, 1907; N. Knight, *Chem. News*, **97**. 122, 190 (oxidation of siderite); G. Steiger, *Bull. U.S. Geol. Sur.*, **413**. 33, 1910; E. T. Allen and J. Johnston, *Journ. Ind. Eng. Chem.*, **2**. 196, 1910 (oxidation of pyrites).

determined. The degree of coarseness is determined by the decomposability of the powder in 15 or 20 minutes by digestion with boiling hydrofluoric acid.[1]

Hillebrand has confirmed these observations, and tried grinding the hard mineral under water and under alcohol, with the idea of cutting off oxygen from the powder during the grinding. Alcohol gave the better results. He showed that it was not merely increased surface which gave rise to the oxidation, but local heating of the grains in contact with the air at the moment of crushing. He therefore recommended the following procedure:—"The coarse powder is covered in the mortar with absolute alcohol that leaves no residue whatsoever on evaporation. The amount used should not be more than enough to form a very liquid emulsion during the operation of grinding. One or two additions of alcohol may be needed if the grinding has to be of long duration. The grinding should be continued in any case until the mass becomes somewhat thick, then the mortar and pestle are left to dry by unaided evaporation of the excess of alcohol; a wide glass tube should be supported above the mortar to keep out the dust without too much impeding air circulation. When supposed to be thoroughly dry, the powder is transferred in its entirety to a watch-glass and placed on the balance pan, where it is to be kept till it is quite evident that no further loss in weight takes place. It is then transferred to the sample tube." But even then, adds Hillebrand, "if a very fine powder must be employed, there seems no way known at present of correcting for whatever oxidation may have taken place during the grinding."

§ 63. Sieving, Lawning, or Screening.

Ground materials are sieved or lawned to make sure that no particles above a certain maximum size are present. Great care must be taken that there be no contamination from the material of which the screens are made. Screens made of the same metal as one of the constituents to be determined are forbidden. Lawns made from brass, phosphor bronze, and silk are in common use in analytical laboratories. Silk lawns are used whenever metallic contaminations are prohibited. Silk lawns are made from the best Italian silk mounted in wooden or metal frames, with or without collecting box and lid (fig. 72). The following are some commercial sizes of silk lawns:—23, 30, 46, 61, 76, 86, 117, 132, 147 apertures per linear inch. The powder should be gently shaken through these lawns in order to avoid contamination. The sieving of powders with silk lawns for the determination of ferrous oxide is condemned by many analysts (page 465), because of the possibility of contamination with silk fibres.

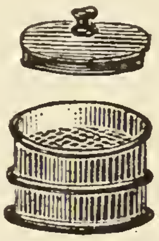
FIG. 72.

In sieving, *all* the powder must pass through the lawn. If only a portion be allowed to pass through, the "knottings" (*i.e.* the residue on the lawn) might have a different composition from that which has passed through. The more brittle constituents of a mixture—*e.g.*, quartz and felspar—will be pulverised first. Thus, Zaleski[2] showed that the dust produced in pulverising granites is richer in felspar relative to quartz and the darker-coloured minerals than the coarser grains of the powder; and with glassy frits, the parts which pulverise first are richer in alkali.[3] Hence, the residue on the lawns must be reground until all passes through.

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[1] If the single treatment does not effect complete decomposition, "which will often be the case" (Hillebrand), the solution, after titration, is allowed to settle, the residue washed once by decantation with water, and again treated with hydrofluoric acid, etc.

[2] S. Zaleski, *Tschermak's Mitt.*, 14. 350, 1895.

[3] T. E. Thorpe and C. Simmonds, *Proc. Manchester Lit. Phil. Soc.*, 45. 1, 1901; *Journ. Chem. Soc.*, 79. 791, 1901.

It is generally advisable to state the size of the mesh of the lawn used in analytical and experimental work. There is some confusion owing to differences in the size of wire, method of weaving, etc. In order that there might be as little confusion as possible, the Institute of Mining and Metallurgy have arranged a set of sieves with a definite size of aperture.[1] Their table follows (Table XIX.).

Table XIX.—The I.M.M. Standard Laboratory Sieve Scale.

Mesh, *i.e.* apertures per linear inch.	Diameter of wires.		Diameter of aperture.		Screening area per cent. holes.
	inch.	mm.	inch.	mm.	
5	0·1	2·540	0·1	2·540	25·00
8	0·063	1·063	0·062	1·574	24·60
10	0·05	1·270	0·05	1·270	25·00
12	0·0417	1·059	0·0416	1·056	24·92
16	0·0313	0·795	0·0312	0·792	24·92
20	0·025	0·635	0·025	0·635	25·00
30	0·0167	0·424	0·0166	0·421	24·80
40	0·0125	0·317	0·0125	0·317	25·00
50	0·01	0·254	0·01	0·254	25·00
60	0·0083	0·211	0·0083	0·211	25·00
70	0·0071	0·180	0·0071	0·180	25·00
80	0·0063	0·160	0·0062	0·157	24·60
90	0·0055	0·139	0·0055	0·139	24·50
100	0·005	0·127	0·005	0·127	25·00
120	0·0041	0·104	0·0042	0·107	25·40
150	0·0033	0·084	0·0033	0·084	24·50
200	0·0025	0·063	0·0025	0·063	25·00

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[1] This subject is discussed in more detail in Vol. II. of this work.

CHAPTER VIII.

SAMPLING.

When conscious choice is permitted to enter into the operation ot sampling, a fair sample will not result, except by a miracle.—W. GLENN.

§ 64. The Problem of Sampling.

A FEW grams of material are sufficient for a chemical analysis, although tons of material may be bought or sold on the result. Large sums of money, too, may be involved in the results of experiments made with but a minute fraction of the total bulk of the material. In such cases it is of fundamental importance to work with samples typical of the whole, since a small error on a gram of material would be multiplied a millionfold when calculated up to tons of material. If the material be perfectly homogeneous, a "grab" sample, taken at random from any part, will be quite representative. In other cases—for instance, a clay bank, or a prospective clay field, or a cargo of bone for moisture, where the amount of moisture might vary from 3 to 13 per cent.—analyses and tests made on "grab" samples may be quite misleading.

Sampling is the art of extracting from a large bulk of material a small portion which shall fairly represent the character of the whole bulk. It would be difficult to over-emphasise the importance of accurate sampling. Indeed, the errors incidental to the process of chemical analysis are sometimes insignificant when compared with the errors involved in bad sampling. It is surprising, to one who realises the importance of this subject, to contrast the care taken in conducting a chemical analysis with the carelessness which prevails in sampling. The analysis of a carelessly selected sample is worth nothing. Many complaints of the failure of chemical analyses can be traced to faulty sampling.

In sampling commercial materials it is necessary to be "on guard" against unscrupulous vendors or manufacturers. They sometimes exercise a diabolical ingenuity in getting a good sample into the analyst's hands when perhaps the bulk of the material is indifferent or bad. Accurate sampling is difficult enough when we have to deal with the natural vagaries of raw materials, but the subject is still more difficult when we are confronted with ingenious artifices meant to deceive. Examples soon accumulate in a laboratory, but inventors are fertile in resource, and the field is always verdant.

The chance or probability of a sample answering expectations might be compared with the chance of drawing the ace of diamonds from a new pack of cards; of throwing a six with a dice, or of tossing "heads" with a penny. The probability of these events is very different, and the probability of selecting the best representative value for material in bulk by means of a grab sample depends upon the nature of the material. The less homogeneous the material the less likely is the grab sample to represent the character of the material in bulk (see size ratio, page 134). Samples selected by a vendor for advertising purposes are here excluded from consideration, because the chance of getting a "first-class result" can sometimes be compared with the probability of throwing a six with a dice loaded for that number.

§ 65. Selecting the Sample.

If the material be in slip—for instance, in checking the composition of a glaze in the dip tub—the material must obviously be thoroughly agitated before the sample is taken, or difficulties will arise owing to settling. A device like that indicated in fig. 73 is useful for withdrawing samples from different parts of a tub or an ark of slip. The end of the tube *A* with the plug *B* pulled tightly into its socket by means of the wire and handle *C* is sunk to the required depth in the slip. The plug is then pushed downwards for a few moments. Slip runs into the lower end of the tube. The plug is then pulled back into its socket, and the tube with the slip inside withdrawn. The slip can be removed in an obvious manner. Metzger[1] has a much more complicated device by which several samples may be taken simultaneously at several different depths.

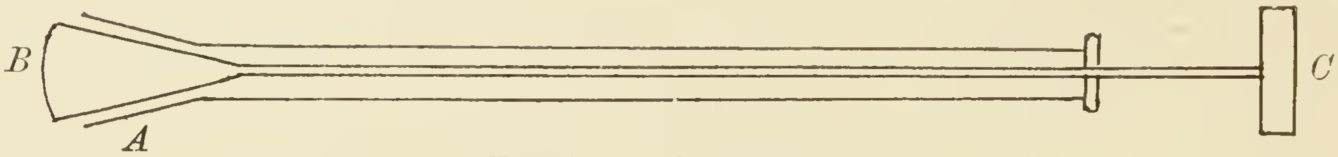

FIG. 73.—Slip sampler.

The sample of "slip" must be dried and then thoroughly mixed. This arises from the fact that clay and glaze slips, on standing, are liable to separate into layers of different composition.

With powdered manufactured or natural products, "grab" samples can be selected from a number of different parts of the stuff in bulk. A cheese scoop is useful for drawing portions from stuff in bins, sacks, etc. Metzger (*l.c.*) has devised a good sampler for this purpose (fig. 74).[2] In the diagram (*a*) it is represented ready for insertion. When inserted it is screwed so that an opening is made for collecting the material to be sampled (*b*). Another screw will close the apparatus ready for withdrawal (*a*).

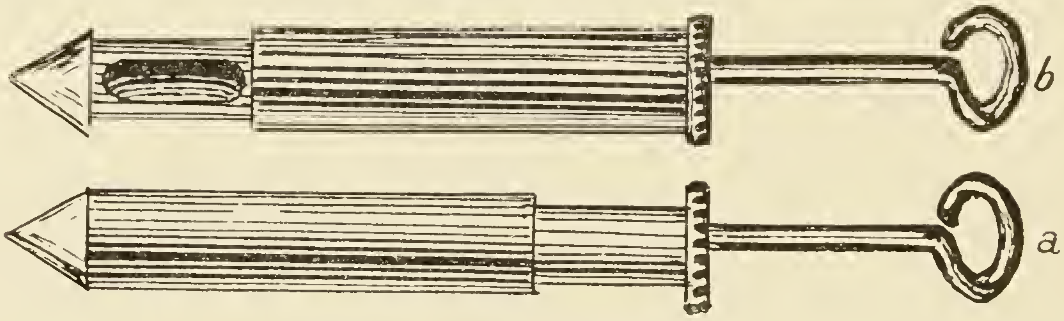

FIG. 74.—Metzger's sampler.

The number and size of the different "grab" samples is determined by the nature and size of the material under investigation. A ship-load of bone, for instance, wants different treatment from a truck-load of clay, a boat-load of felspar, or a load of borocalcite.

Accurate sampling can only be performed when the materials can be pulverised. A perfect method of sampling must eliminate the personal factor, and work with machine-like precision. This is quite easy with powdered materials intimately mixed, and the "time-sampling machines" which grind and periodically select a fraction of the whole do this work very well. This kind of sampling is seldom practicable in dealing with clays and potter's materials. In sampling many ores, 5 per cent., that is, one-twentieth of the whole, is supposed to be selected in portions of equal weight and at frequent intervals. If the material is being delivered in shovels, every twentieth shovel is sometimes put on one side; if delivered in barrows, every twentieth barrow; if in sacks, every twentieth sack, and so on, according to the nature of the material to be sampled. With cargoes of some materials "one-in-fifty" will be ample.

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[1] P. Metzger, *Zeit. anal. Chem.*, 39, 791, 1900 ; O. Steinle, *Zeit. angew. Chem.*, 5. 584, 1892 ; A. Gawalovski, *Allgem. Österr. Chem. Tech. Ztg.*, 6. 197, 1889.

[2] R. Kroupa, *Berg. Hütt. Ztg.*, 48. 301, 1887 ; J. T. Stoddard, *Journ. Anal. App. Chem.*, 4. 34, 1890.

§ 66. Reducing the Bulk of the Sample.

A large sample must be reduced in bulk before it can be treated in the laboratory. The reduction may be done by hand or by machine. There are at least five methods available for reducing the sample to a convenient bulk for treatment in the laboratory: (1) fractional selection; (2) quartering; (3) channelling; (4) split shovelling; and (5) riffling. In machine sampling the material may be (1) divided into two or more unequal streams, and one or more streams reserved for the sample (split-stream samplers); (2) the whole of the stream may be taken off intermittently (time samplers).

(1) *Sampling by Fractional Selection.*—The selection of 5 per cent. of the total bulk of the material (heap A) to be sampled as indicated above is an illustration of this method of sampling. The first sample (heap B) is ground, if necessary, into grains on average, say, one-twentieth the size of the first sample, and every twentieth shovel or barrow-load collected into another heap, C; this is again ground and subdivided until one or two hundredweights are obtained in a heap, say D. The operations are summarised as follows:—

A = 1000 tons of a cargo of material to be sampled;
B = 50 tons in first fraction;
C = 2·5 tons in second fraction;
D = 0·125 tons or 280 lbs. in the third fraction.

Hence, if w represents the weight of material in the mass to be sampled, the nth fraction will have $w(0{\cdot}05)^n$th part of the original bulk.

(2) *Sampling by Coning or Quartering.*[1]—A homogeneous pile of the material is built up as a cone about a real or imaginary rod as centre. Every shovelful of the material is thrown directly on top of the growing cone, so that it runs and spreads more or less evenly down the sides. As a matter of fact, the fine material has a tendency to accumulate about the centre of the cone, while the coarse material rolls down the sides and an almost imperceptible sorting occurs (see fig. 78). The operator, in building up the cone, drops the shovel of material on top of the cone by giving the shovel a jerk upwards (just over the apex of the cone), and then another jerk downwards and outwards as indicated by the arrow, *a*, fig. 75. The material falls downwards on the apex of the cone, *b*, fig. 75. With experienced men, the circumference of the cone, when finished, will be nearly circular. The cone is then spread out into a "pancake" by means of shovels working from the centre to the periphery round and round the cone (fig. 76). The pancake is then separated into quarters by means of boards or steel blades (fig. 77), pointing, say, north and south, and east and west. If the N.E. and S.W. quarters are rejected, the N.W. and S.E. quarters are piled into another cone, and again quartered. Thus 200 lbs. would be reduced by

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[1] W. Glenn, *Trans. Amer. Inst. Min. Eng.*, **20**. 155, 1891; C. M. Roberts, *ib.*, **28**. 413, 1898; P. Johnson, *Eng. Min. Journ.*, **53**. 111, 132, 1892.

the first cut to 100 lbs. A second cut would reduce this to 50 lbs. And generally, starting with a weight w of material, the nth cut gives by quartering

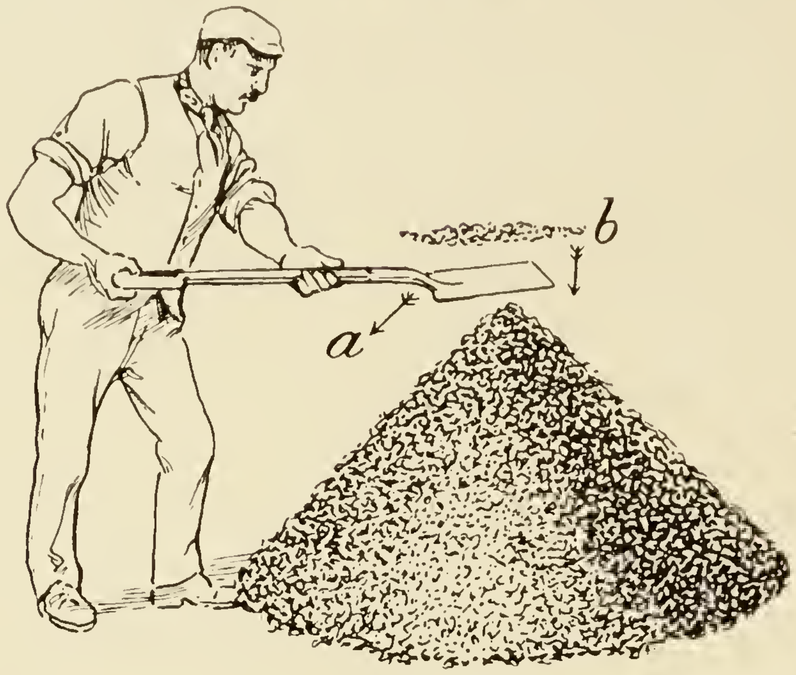

Fig. 75.—The cone almost ready for flattening.

a weight $w(0{\cdot}5)^n$th of the original weight w. Thus, starting with 200 lbs., the tenth cut will give $200 \times (0{\cdot}5)^{10} = 0{\cdot}195$ lb.

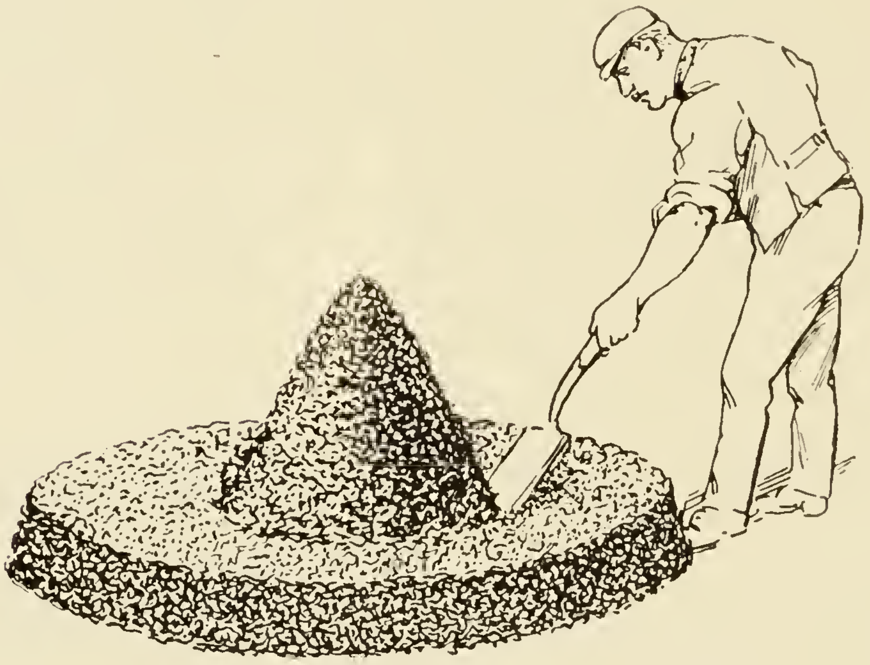

Fig. 76.—The cone partially flattened.

Two men can reduce a ton of material down to a few pounds in two or three hours. Perfect mixing, accurate subdivision, thorough cleanliness are essential to success in all the methods for reduction.

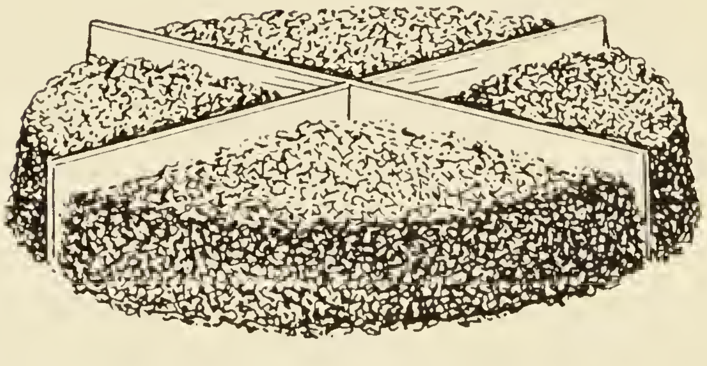

Fig. 77.—"Pancake" cutting.

It will be noticed that owing to the accumulation of the fine material towards the centre, if the apex of the cone be deliberately or accidentally deflected while being built, it is possible and probable that in levelling, the first layers, at the bottom of the cone, will lie wholly in one quarter, and thus the proportion of fine material in that quarter will be abnormally high. The effect of imperceptibly drawing the centre of the cone on the relative proportion of fine and coarse material will be evident from fig. 78 (after Brunton), which is a photograph of a cone built up in actual sampling practice, bisected by a sheet of glass, and one-half of the cone removed. The diagram shows well the structure of a cone with a drawn centre.[1]

(3) *Sampling by Channelling.*[2]—The material to be sampled is spread out in the form of a square about 4 inches thick. Parallel grooves—say 1 foot apart—are cut across the cake; and then another set of grooves at right angles to these. The process is repeated with the material so cut from the square. The method is slow and inaccurate, for coarse pieces may fall into the grooves as they are being cut.

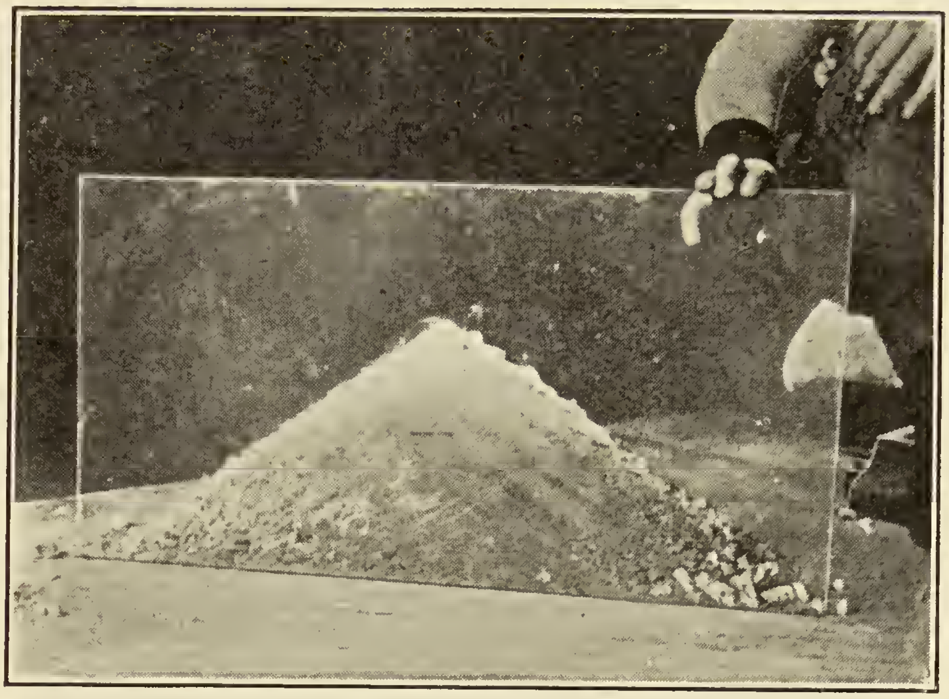

Fig. 78.—"Drawn" cone. (After J. D. Brunton.)

(4) *Split-shovel Sampling.*—One workman (left, fig. 79) throws the material from a broad shovel upon a narrow U-shaped scoop-like shovel held by another workman (right, fig. 79) over a car or wheelbarrow (fig. 79). The material which remains on the shovel is retained. When a pile of this has accumulated in the wheelbarrow, it may be further reduced in bulk by repetitions of the process.

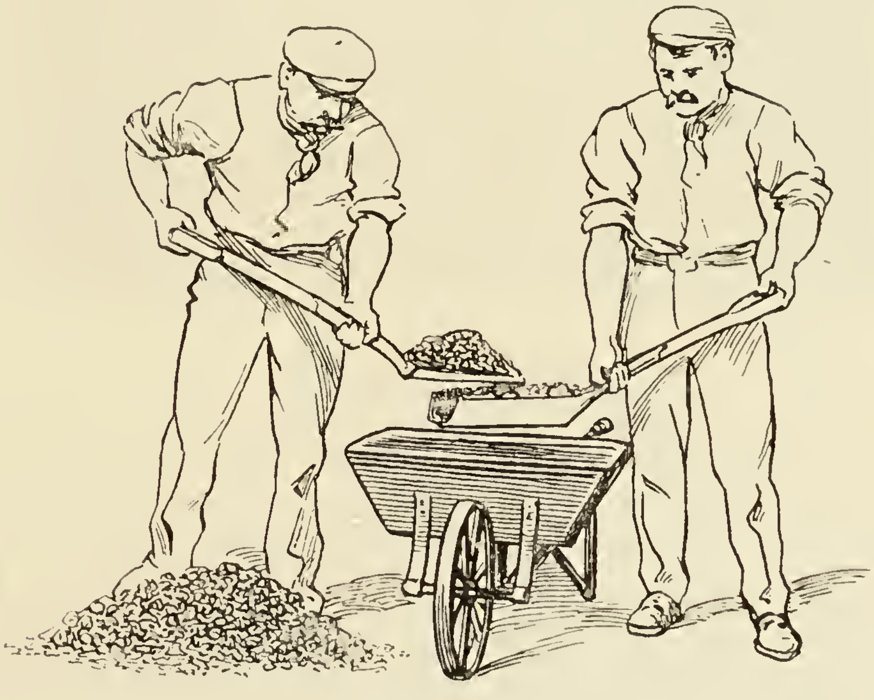

Fig. 79.—Sampling by the U-shovel or the split shovel.

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[1] J. D. Brunton, *Trans. Amer. Inst. Min. Eng.*, **40**. 675, 1909.

[2] F. A. Lowe, *Eng. Min. Journ.*, **31**. 203, 1881; W. Glenn, *Trans. Amer. Inst. Min. Eng.*, **20**. 115, 1891. For a mechanical device for cone-sampling, see C. W. Kneff, *Journ. Ind. Eng. Chem.*, **4**. 682, 1912.

There are several different types of split shovel.[1] Some have a series of such scoops on one shovel, with spaces and scoops equal in width.

(5) *Riffle Sampling.*—The riffle consists of a series of grids arranged to form alternate series of troughs and spaces. When the material to be sampled is spread by means of a shovel over the riffle, supported over, say, a wheelbarrow, part of the material passes into the barrow, and part remains in the troughs. When the troughs are full, the contents are put on one side for further trial. That which passes through the grids is rejected. There are several modifications. In Jones' riffle the troughs are inclined, and slope in opposite directions. There are no spaces. The material when spread over the troughs (2 in. wide) is broken into two streams passing in opposite directions, and each stream is collected in a suitable receptacle. The riffle is usually employed for cutting down samples for the laboratory when the amount is too small for the larger mechanical samplers.

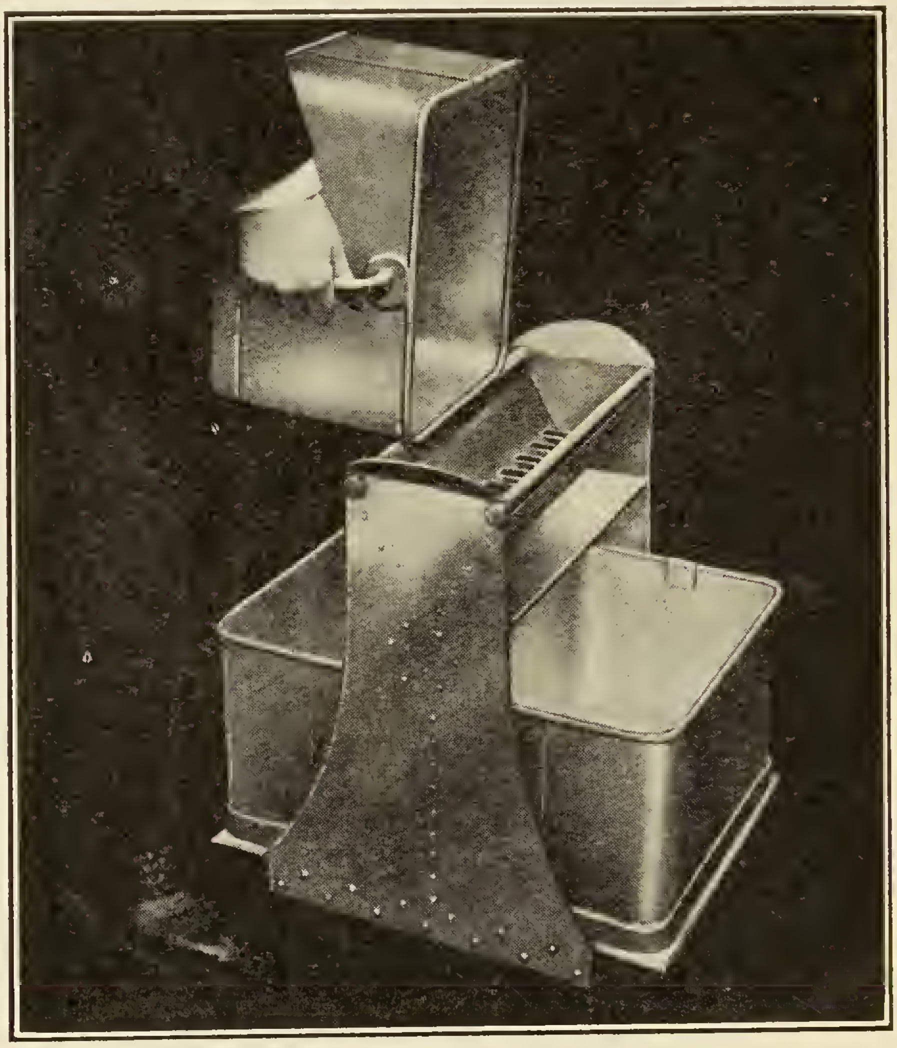

Fig. 80.—Taylor and Brunton's split-stream sampler.

Taylor and Brunton's splitter (fig. 80) is a modification in which numerous small spouts are arranged across the entire width of a large gutter, so that the main stream of the material, poured into the gutter, is divided into a number of smaller streams. The odd-numbered streams may be deflected to, say, the right, the even-numbered streams to the left. The material which collects on one side is rejected; the other—the sample side—is retained. The method of pouring will be obvious from fig. 80. The operations are repeated on the material which has passed through the divider as often as desired.

These samplers reduce the volume 50 per cent. each time the material is treated, as is the case in quartering. It is important to thoroughly mix the material collected on the sample side before it is passed through again.[2]

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[1] J. D. Brunton, *Eng. Min. Journ.*, 51. 718, 1891; S. A. Reed, *School Min. Quart.*, 3 253, 1882.

[2] J. D. Brunton, *Trans. Amer. Inst. Min. Eng.*, 40. 567, 1909.

§ 67. Machine and Automatic Sampling.

Split-stream Samplers.—In Clarkson's divider,[1] the material is poured into a funnel where it is split into six similar streams (fig. 81). The material before it is placed in the funnel is supposed to have been ground to pass at least an 8's lawn. It is fundamentally important in all systems of sampling to make sure that the "sample" and "reject" are of the same composition.

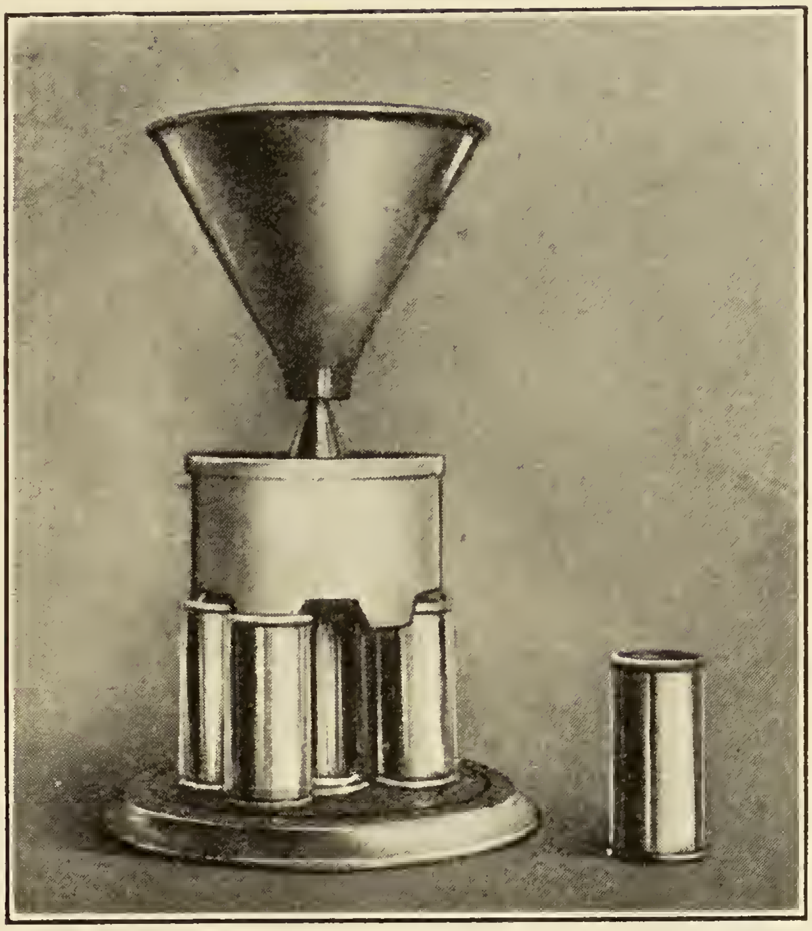

Fig. 81.—Clarkson's split-stream sampler.

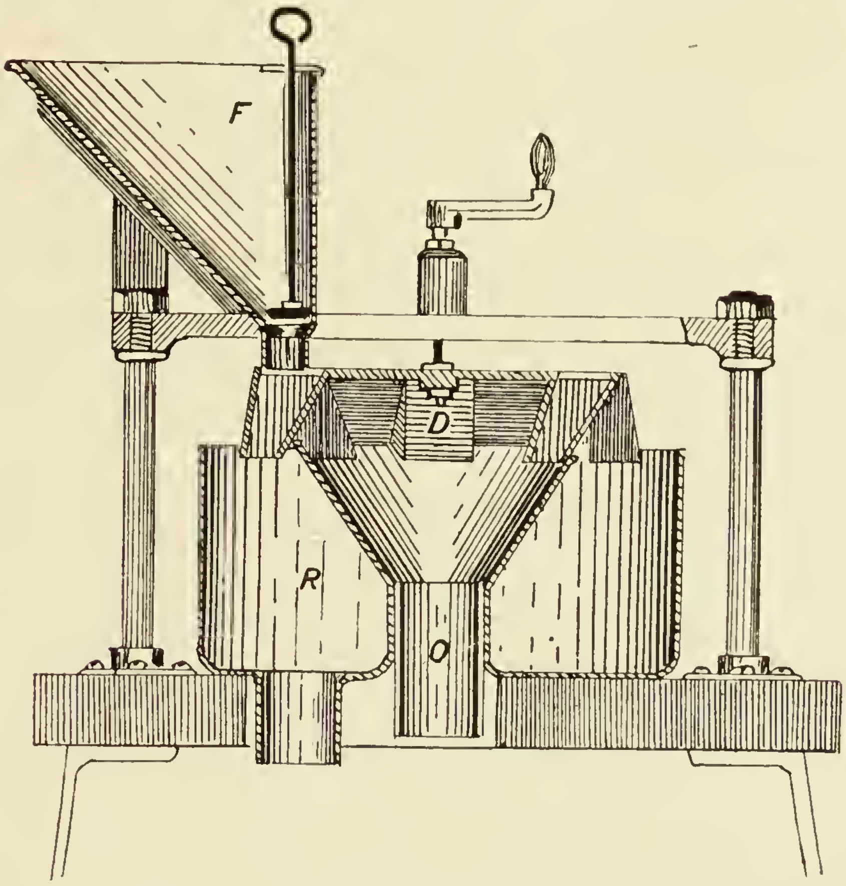

Fig. 82.—Bridgman's time sampler.

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[1] T. Clarkson, *Journ. Soc. Chem. Ind.*, 12. 214, 1894.

There are many other types on the same principle. In some, a series of funnels are superposed one above the other, so that a fraction of the stream is rejected and another fraction is further fractioned as it passes on to the subjacent funnel, *e.g.* F. W. Braun's "Umpire" sampler,[1] which is excellent.

Time Samplers.—In the time-sampling machine, the whole of a falling stream of the material is periodically deflected during a portion of the time. This eliminates one fault with split-stream samplers—where the sizes of the grains are never evenly distributed across the stream. In some, on a large scale, the material is alternately subdivided and crushed from the coarsest down to the finest powder. The machines are represented by Snyder's time sampler;[2] the Vezin time sampler;[3] and the Brunton time sampler. H. L. Bridgman's time-sampling machine[4] is a compact little instrument occupying but 14 square inches. It has a divider *D* set in motion by clockwork or any other power (fig. 82). *F* is a funnel with a receptacle *R* for the fraction separated from the material being sampled. The portion rejected passes through the discharge orifice *O*. The material runs from the hopper in a continuous stream to the divider, which cuts the stream eight times during one revolution. Four of these are delivered into the discharge orifice, and four are delivered into the receptacle.

§ 68. Reducing the Grain Size and Bulk of the Material during Sampling.

The process of sampling involves two operations: (*a*) reducing the bulk of the material as indicated in the preceding sections; (*b*) reducing the size of the grains of the material. The important factors in accurate sampling are: (1) the relation between the amount of material selected as the sample and the original bulk of the material to be sampled—the bulk ratio; (2) the relation between the coarseness of the grain and the amount—the size ratio (sampling); (3) the relation between the size of the grain and the amount isolated at each stage of quartering, etc.—sizo ratio (quartering).

(1) *The Relation between the Bulk of the Sample and of the Material to be sampled.*—The greater the ratio between the weight of the sample and the weight of the whole of material sampled; that is, the greater the ratio,

$$\frac{\text{Weight of sample}}{\text{Weight of material in bulk}} = \text{Bulk ratio},$$

the greater the probability of the sample representing the true character of the material under investigation. This is illustrated by the following table, due to Bailey:—

Table XX.—Relation between Errors in Sampling and Size of Sample.

Bulk ratio.	Percentage error—sample and bulk.
1 : 100	1·4
2 : 100	0·8
5 : 100	0·6

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[1] F. W. Braun, *U.S. Pat. No.* 682528, 1901.

[2] F. T. Snyder, *Canada Min. Rev.*, **17**. 43, 1898.

[3] H. A. Vezin, *Trans. Amer. Inst. Min. Eng.*, **26**, 1098, 1896.

[4] H. L. Bridgman, *Trans. Amer. Inst. Min. Eng.*, **13**. 639, 1884; **20**. 416, 1891; *U.S. Pat. No.* 553508, 1896.

(2) *The Relation between the Grain Size and the Weight of the Sample.*—The smaller the ratio between the weight of the largest pieces and the total weight of the sample; that is, the smaller the fraction,

$$\frac{\text{Weight of largest pieces in sample}}{\text{Total weight of sample}} = \text{Size ratio},$$

the more likely is the sample to represent the character of the material in bulk. Bailey's experiments[1] on sampling coal (with 5 per cent. ash) illustrate this point very well. He found that if the error is to be less than 1 per cent., the relation between the grain size of the sample and the weight of the largest pieces in the coal must be near that indicated in the following table, due to Bailey:—

Table XXI.—Relation between Fineness of Bulk Material and Size of Sample.

Weight of largest pieces in lbs.	Amount of sample not less than (lbs.)
6·7	39,000
2·5	12,500
0·75	3,800
0·38	1,900
0·24	1,200
0·12	600
0·046	230
0·018	90

Under these conditions the sample is less likely to be disturbed by an accumulation of abnormally fine dust or coarse material.

(3) *The Grain Size of each Fraction (Quartering).*—The relation between the grain size and the amount to be isolated at each stage of the quartering is an important factor, as will be obvious from the preceding notes on the relation between the grain size and the amount to be selected as a sample. Continuing the experiments just described, Bailey found that in order to get the deviations in the composition of the ash of coal within the limits stated, it was necessary to reduce the sample before quartering or fractioning to the grain size indicated in the following table:—

Table XXII.—Relation between Fineness of Sample and Bulk of Material.

Weight of fraction in lbs.	Size to be crushed. Diam. in inches.
7500	2
3800	1·5
1200	1
460	0·75
180	0·5
40	0·425 (2's lawn)
5	0·20 (4's lawn)
0·5	0·1 (8's lawn)
0·25	0·076 (10's lawn)

---

[1] E. G. Bailey, *Journ. Ind. Eng. Chem.*, **1.** 161, 1909; **2.** 543, 1910; F. C. Weld, *ib.*, **2.** 426, 1910; F. Fischer, *Stahl Eisen*, **32.** 1408, 1912; W. B. Blyth, *Min. Eng. World*, **37.** 613, 1912.

According to Bailey, if the coal be crushed to a size 2-inch grain, do not subdivide to a fraction less than 8300 lbs. without further grinding; 4-inch mesh for not less than 1100 lbs., etc., as indicated below:

Size of lawn	2	4	8	10	20's
Minimum amount . . .	8300	1100	120	55	3 lbs.

Of course the best value for the bulk and size ratios indicated above will vary with the nature of the material and the degree of accuracy demanded in the sampling. In the absence of data for particular materials, the preceding data will serve as a guide in determining these factors.[1]

To summarise, good sampling involves:

(1) Adequate mixing;
(2) Impartial selection;
(3) Proper grinding.

There is always a danger in applying rules blindly. The exercise of common sense, guided by these three principles, is necessary to cope with the different problems which arise from time to time. All the preceding discussion would be misleading if the object of the investigation were to determine the composition of a specific mineral. In that case the purpose would probably be best served by very carefully isolating as clean and as pure a crystalline fragment as possible. All associated impurities, foreign matter, and all altered fragments should be excluded. Neglect of this precaution would render it necessary to admit the existence of innumerable varieties of a particular mineral.[2]

§ 69. The Receipt and Dispatch of Samples.

In discharging a cargo of bone ash, the "English Form of the Hamburg Contract" specifies:—

> Regular samples shall be drawn from each day's quantity of Ash discharged, and after these samples have been sufficiently mixed, four large bottles shall be filled and sealed, which shall serve as MOISTURE SAMPLES for the $\frac{\text{parcel}}{\text{cargo}}$. The rest of the landing sample shall be ground sufficiently fine to pass through a sieve of 50 holes per square centimetre, of which ground sample there shall be filled and sealed four large glass bottles which shall serve as QUALITY SAMPLES.
>
> All this to be done under the superintendence of Sellers and Buyers or their representatives. Each appointed Chemist shall receive one MOISTURE SAMPLE for the determination of MOISTURE, and one QUALITY SAMPLE for the determination of MOISTURE AND PHOSPHATE OF LIME, and, in ascertaining the percentage of Phosphate of Lime in the QUALITY sample, the calculation shall be based on the percentage of Moisture in the $\frac{\text{parcel}}{\text{cargo}}$ as shown by the MOISTURE SAMPLE.

Samples for analysis or testing should be clearly and distinctly marked;

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[1] For papers on the theory of sampling see P. Argall, *Trans. Amer. Inst. Min. Eng.*, **31**. 235, 1902; D. W. Brunton, *ib.*, **25**. 826, 1895; S. H. Pearce, *Chem. Met. Soc. S A.*, **2**. 155, 1898; S. A. Reed, *School Min. Quart.*, **3**. 253, 1882; **6**. 351, 1885; A. D. Hodges, *Eng. Min. Journ.*, **52**. 264, 1891; V. Samter, *Chem. Ztg.*, **32**. 1209, 1224, 1250, 1908; C. Geissler, *ib.*, **23**. 43, 1058, 1899; *German Pat. No. D.R.P.* 100067, 1898; 100516, 1898; O. Bender, *Zeit. anal. Chem.*, **48**. 32, 1909; *Zeit. Berg. Hütt. Sal.*, **55**. 1, 1907; F. Janda, *Oester. Zeit. Berg. Hütt.*, **52**. 547, 561, 577, 1904; J. A. Barral and R. Duval, *Dingler's Journ.*, **217**. 246, 1876; M. L. Griffin, *Journ. Soc. Chem. Ind.*, **24**. 183, 1905; W. Glenn, *ib.*, **17**. 123, 1898; C. E. Stromeyer, *Pract. Eng.*, **44**. 781, 1911; L. T. Wright, *Chem. Eng.*, **13**. 30, 1911; A. C. Fieldner, *ib.*, **17**. 50, 1913; M. Webber, *Min. Scientific Press*, **102**. 846, 1911.

[2] For the methods available for isolating minerals from clays, see Vol. II. of this work.

and be securely packed so that there is no possibility of contamination during transit.[1]

In disputes on the quality of materials, the sampling should be performed in the presence of the seller's and buyer's representatives. Three 8-oz. bottles should be filled with, say, the powder in question, and both representatives should put their seals on the bottles and sign an account of the taking of the sample. The bottles should have a label stating what the contents are, the name and address of the senders, and a distinguishing mark—number or letter.[2] One bottle may be sent to an analyst agreed upon by both representatives; or one bottle may be sent to the analyst selected by the buyer, and one bottle to the analyst selected by the seller. The remaining bottle or bottles are reserved for verification in case the two analysts differ appreciably in their results.

In some cases, *e.g.* the purchase of iron ore, bone ash, etc., it is the practice to refer a sample to the "buyer's chemist" and a sample to the "seller's chemist." If these differ by less than, say, 1 per cent., the material is bought on the mean of the two results; but if the results differ by more than the agreed 1 per cent., it is the custom to send the sample to a third chemist as referee, and to take the mean of the two nearest results. For bone ash, the "English Form of the Hamburg Contract" specifies that the third chemist shall only be called in when the results by the seller's and the buyer's chemists have "a difference of over 2 per cent. of tribasic phosphate of lime."

The chemist who receives the sample registers the date of arrival, the professed nature of the sample, and the marks on the seals. A formal acknowledgment of the receipt of the sample should be sent, say:—

> I hereby acknowledge the receipt of ... specimens of ....
> ....
> Packed in..
> Nature of seal...
> Marked...
> Laboratory number..
> Purpose..
> Charge ....
> Date received..
>
> ....
> Director of Laboratory.

The whole mass is then emptied from the bottle on to a sheet of white paper[3] and sifted.[4] If any particles do not pass through the sieve, they must be ground until all passes through. The mass is then mixed with a spatula and re-sifted through a coarser sieve. A portion is then taken for analysis, and the remainder is returned to the bottle. The result of the analysis is recorded on a certificate somewhat as follows:—

---

[1] I have known a batch of firebricks which (so far as I could see) must have been saturated with salt during transit from the sender to the receiving chemist.

[2] In case of a seizure of, say, a glaze sample by the Inspector of Factories, the material should be thoroughly agitated and three nearly equal portions removed in the presence of the proprietor or his representative. The corks of the bottles should be pressed level with the glass; sealing wax placed on the top of the cork (or string if the sample should be a powder wrapped in paper), so that the package cannot be opened without breaking the seal of wax. A distinctive seal should then be impressed on the wax, and each package labelled with distinctive and similar labels showing the name of the firm, where taken, date of sampling, date sent to analyst, distinctive number or letter, and the nature of the sample.

[3] The analyst should inquire if the sample has been divided into two or three portions when sampled. If not, the sample should be divided into two parts nearly equal, and one part should be sealed and labelled as indicated in the text. This sample may be reserved or returned either on receipt of the sample or when the certificate is supplied. Slop glazes are dried as indicated on page 330.

[4] The mesh of the sieve must be determined by the nature of the powder.

References to Laboratory Number.........
I hereby report that the specimen of ...., marked ....,
sampled by ...., and received from ....
on ...., has been duly | analysed | in this laboratory
tested
with the following result;

....
Director of Laboratory.

No responsibility is taken for the accuracy of the sampling unless it has been done under our own supervision.

§ 70. Sampling Beds of Clay.

Another type of sampling is sometimes required. To find if it is advisable to install plant for working a natural bed of clay, it is necessary to make a somewhat close approximation as to the amount of clay available, as well as to determine the nature of the clay, possible market, cost of transport, fuel, labour, etc., etc. Here we are alone concerned with making an estimate of the amount of clay and the collection of samples for investigation.

In sampling an unworked bed of clay near the surface, a hole may be sunk through the different strata well into or through the clay under investigation, and 28-lb. grab samples taken from the exposed face. It is well to keep for reference small samples of the different superincumbent strata. Care must be taken in digging and sampling the hole not to mix fragments from one stratum with those of another. The distance between the original locus of the different samples and the surface should be measured and recorded on and in the boxes or bags in which the different samples are preserved. If the clay under investigation is any great distance from the surface, this procedure would be laborious if it were required to explore the thickness and extent of the clay. Many of the well-known types of borer bring a core to the surface with much less labour than is involved in digging holes, as described above. The type of borer to be employed is largely determined by the hardness of the different strata and the depth of the required boring. Two men can conveniently work one of H. Meyer's borers to a depth of 30–50 feet in a few hours.[1] Fraenkel's borers can be sunk about 12 feet by one man in a few hours in ordinary surface clays. Bore-holes have been driven by power over 7350 feet.[2] The cost for the deep-seated clays would generally be prohibitive, although bores ranging up to 500 feet are common enough. When a series of cores properly measured has been obtained, the nature of the clay can be investigated by methods to be described later.

Much naturally depends on the geological character of the bed in question. The continuity, thickness, and nature of a bed of fireclay in, say, the coal measures in a given area can often be predicted with a high degree of probability by a geologist provided with particulars of the same stratum in part of the prescribed area. Hence a boring within the prescribed area can only demonstrate what was almost a certainty.[3] A skilled geologist may be able to correlate the stratum under investigation with another known stratum elsewhere. The nature of certain strata frequently persists throughout wide areas; for instance, the peacock marl (N. Staffs.), the Old Mine clay (Stourbridge), Oxford clay, London clay, etc. Other strata, and even the clays just mentioned, may vary in an apparently erratic manner in certain localities. A prudent man, therefore, will try to estimate what amount and what quality of clay is available.

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[1] A. Fauck, *Anleitung zum Gebrauche des Erdbohrers*, Leipzig, 1877; Suppl., 1899; H. Bansen, *Das Tiefbohrwesen*, Berlin, 1912.

[2] With rotary diamond drills—2003·34 metres at Paruschowitz (Upper Silesia)—*B.A. Rep.*, 67, 1901; with percussion drills—5570 feet at Sperenberg (about 25 miles south of Berlin)—H. W. Bristow, *Geol. Mag.*, 4. 95, 1875; B. Jäger, *Zeit. Berg. Hütt. Sal.*, 59. 89, 1911.

[3] The process of boring may then be compared with interpolation in mathematics. The possibility of "faults," etc., may render an extrapolation futile and stultify a prediction.

Sampling and boring is somewhat costly work, but, when properly done, it gives a clear idea of the extent and nature of a hidden bed of clay, and it prevents awkward mistakes, such as the erection of the kilns, machine sheds, etc., over what might be the best part of the clay.[1] Exposures and cuttings in a given neighbourhood may furnish enough information as to the amount of clay available in a given area without any need for an elaborate system of boring.

When a series of borings have been obtained, they may be recorded in the following manner. For convenience we apply the method to a particular problem. A few years ago, a valuable plastic clay 15 feet thick gave signs of tapering off. A series of borings 20 feet deep were made, and it was proved that the clay seam "petered out" between 40 and 50 feet away from the working face. A new seam of a somewhat similar plastic clay was "struck" below a 10–20 feet seam of a sandy clay. In boring systematically to find the extent of the new seam, what appeared to be the old seam was taken up not far from where it had tapered off. In boring, the "field" was divided into a series of imaginary rectangles resembling a chess-board. A boring was made at every corner. With the data so obtained diagrams were drawn to scale representing sections through the different strata in particular directions. One such section is illustrated in fig. 83. This is drawn from the borings Nos. 5, 6, 7, 8, which were :—

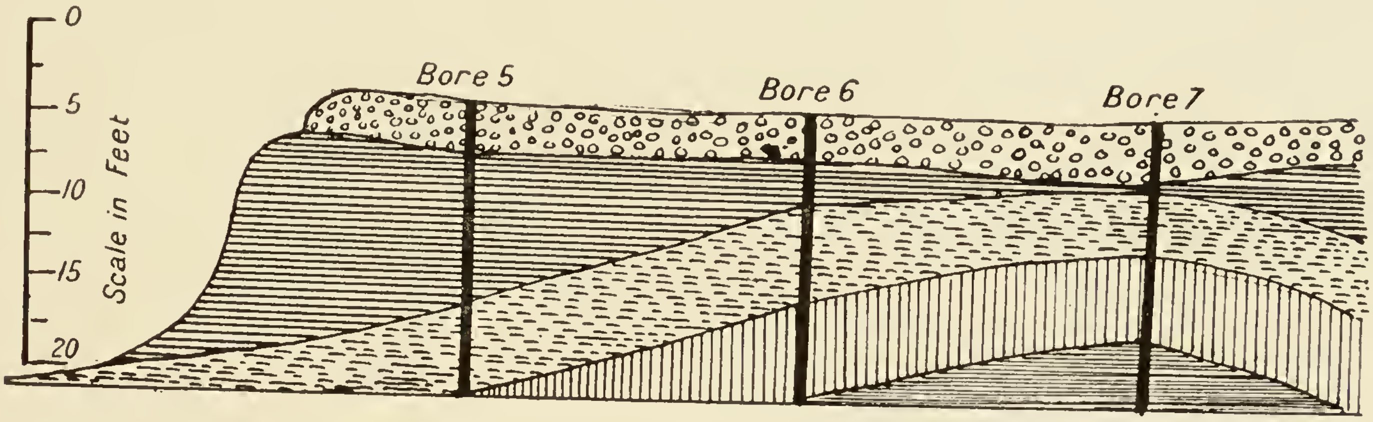

FIG. 83.—Section constructed from borings.

	No. 5.	No. 6.	No. 7.	No. 8.
	ft. in.	ft. in.	ft. in.	ft. in.
Overburden . .	2 8	2 10	3 0	2 5
Plastic clay . .	9 7	2 11	0 2	6 0
Sandy clay . .	7 8+	6 0	4 8	4 5
Plastic clay B. .	...	7 10+	5 0	6 2
Sand . . .	...	...	6 0+	3 2+

The distance apart and depth of the borings for each particular "field" must be determined by the circumstances of the case, and the advice of a geological expert may be required.

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[1] An instructive example occurs at an abandoned clay pit near Cobridge (Staffs.).

§ 71. The Commercial Value of Clay Deposits.

In order to evaluate a clay deposit, it is necessary first of all to determine the commercial value of the goods to be made from the clay, which, after all, reduces to the present market value of a cubic foot of the clay. Due consideration is of course paid to the district, facilities for transport, cost of fuel, etc. In some inaccessible districts land covering a first-class clay might have no more value than ordinary agricultural land, owing to lack of facilities for transport, cost of fuel, etc. In the second place, it is necessary to determine how much clay is available. In the third place, an approximate estimate must be made of the yearly consumption of the clay, and consequently also how many years the seam of clay will last at the estimated rate of consumption. We are then in a position to deal with the problem by arithmetic.[1]

Let R represent the estimated value of the clay consumed per annum ; r, the rate of compound interest for the money were it invested at the current rate ; and n, the estimated number of years the clay is likely to last before the seam, or the given portion of a seam, is exhausted. The regular rules for compound interest show that the present value, P, of the given field of clay can be represented by the expression :

$$P = R\frac{p^n - 1}{p^n(p - 1)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where, for convenience, we have written

$$p = \frac{100 + r}{100} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To illustrate by example, suppose that 10,000 cubic feet of clay be removed each year ; that 1,000,000 cubic feet of clay are still available.[2] The clay is worth $\frac{1}{4}$d. per cubic foot. The rate of interest is $3\frac{1}{2}$ per cent. What is the present value of the field of clay? Here, $r = 3{\cdot}5$; hence, from (2), $p = 1{\cdot}035$. The 1,000,000 cubic feet of clay will last 100 years if 10,000 cubic feet be removed per annum. Hence, $R = 10{,}000 \times \frac{1}{4} = 2500$d. Consequently, from (1),

$$P = 2500\frac{(1{\cdot}035^{100} - 1)}{1{\cdot}035^{100}(1{\cdot}035 - 1)} = £288, \text{ 1s. 6d.}^3$$

It is then possible to decide whether it is better to pay an annual royalty for the clay, to pay a proposed rental, or to purchase the field at a stated price.

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[1] E. Tschenschmer, *Tonind. Ztg.*, **14.** 121, 139, 1890 ; *Brit. Clayworker*, **18.** 279, 1910.

[2] The estimation of the cubic contents of a given seam is simple arithmetic—solid mensuration—when the borings are known.

[3] Log $p^n = n \log p$. Hence 100 log 1·035 = $100 \times 0{\cdot}0149403 = 1{\cdot}49403 = \log 31{\cdot}191$, or $1{\cdot}035^{100} = 31{\cdot}191$.

CHAPTER IX.

THE REAGENTS.

§ 72. Testing the Reagents.

The purity of the reagents and of the distilled water for analytical laboratories should not be taken on trust.[1] The glass containers may contaminate liquid reagents with iron, potassium, sodium, silica, calcium, and alumina by the dissolution of the glass; and zinc may be derived similarly from Jena glass and "nonsol" glass vessels. Iron is common in acids transported in carboys. Small flakes of iron may scale from the blowpipes used by the glass-blower, and this may not be removed or noticed in washing these vessels. Reagents may be contaminated from their contact with the vessels—tanks, stills, condensers, crystallising dishes, etc., made from lead, silver, copper, iron, aluminium, nickel, zinc, tin, porcelain, glass, etc.—used in the process of manufacture. Thus, not only may the ordinary constituents of glass be present, but nickel may be found in caustic alkalies, copper and aluminium in acetic acid, zinc in barium carbonate,[2] selenium and iron in hydrochloric acid,[3] and lead in organic acids and in hydrofluoric acid. The latter has also been known to contain potassium sulphate and ammonium and sodium chlorides. Impurities may also be derived from the raw materials used in the process of manufacture. In fact, it is almost impossible to free some reagents from certain impurities except at a very high cost. For example, iron, alumina, and silica are found in all but the highest-priced grades of caustic alkalies and alkaline carbonates; calcium is very difficult to remove from ammonium oxalate; nickel from cobalt; iron and lead from copper; free acid from ferric salts; ammonia from magnesium chloride; etc.[4] All this is mentioned to emphasise the fact that *constant vigilance is the price of successful work.* Many impurities might easily escape detection. For instance, selenium in hydrochloric acid; sulphates in platinum chloride; lead in ammonia; phosphorus in ammonium chloride and nitrate; and calcium in ammonium oxalate.[5] Hence, in quantitative analysis particularly, the reagents are best tested by blank or dummy analyses.[1] The blank analysis does not necessarily give absolute certainty, because the reactions without the substance are not necessarily the same as with the substance. In most cases, however, the blank analysis is an excellent and reliable method of testing the purity of reagents, and it frequently furnishes a means of correcting the results of the analysis proper.

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[1] The "analysed" chemicals supplied by many of the better-class makers are generally very good.

[2] R. Wegscheider, *Zeit. anal. Chem.*, **29.** 20, 1890.

[3] W. B. Hart, *Chem. News*, **48.** 193, 1883.

[4] J. W. Shade, *Journ. Amer. Chem. Soc.*, **28.** 1422, 1906; J. T. Baker, *Journ. Ind. Eng. Chem.*, **I.** 464, 1909.

[5] C. Krauch gives the regulation tests for impurities in reagents in his *Die Prüfung der chemischen Reagentien auf Reinheit*, Berlin, 1896 (J. A. Williamson and L. W. Dupre's translation, New York, 1902); E. Merck, *Prufung der chemischen Reagenzien auf Reinheit*, Darmstadt, 1912; or E. White, *Analytical Reagents*, London, 1911. I am here reminded that one of the county councillors, with the idea of "testing the analyst," introduced a "poison" into some beer and sent it to the county analyst to report on adulterations (*Chem. News*, **54.** 254, 1886). The analyst reported the sample to be "genuine unadulterated beer." The analyst was right. The poison was not an adulteration. Had the analyst been asked to test for every conceivable admixture, the "bill of costs" would have startled the councillor. I mention this because it illustrates what grotesque notions are rife as to the functions of an analyst working for commercial purposes at a specified (minimum) fee.

§ 73. Bottles for Reagents.

In a laboratory where a number of workers use the same bottles, particular care must be exercised. Errors might easily creep into the work from an interchange of stoppers, placing stoppers on the working benches, mistakes in filling and weighing out the reagents, etc. The necks and mouths of all the bottles should be kept clean. The bottles and the stoppers should be numbered so that no confusion is possible. The "mushroom" stopper (fig. 84) is not sufficient to protect the mouth and lip of the bottle from dust, and when these flat stoppers are "stuck" they are unusually difficult to loosen.[2] F. F. Jewitt has designed a stopper with a pendant flange (fig. 85), with the idea of protecting the mouth and lip of the bottle from dust. These bottles are at present made in two sizes —125 c.c. and 250 c.c., with enamelled labels. The 250-c.c. bottles cost 16s. 6d. per dozen. These stoppers are also very difficult to loosen when stuck.

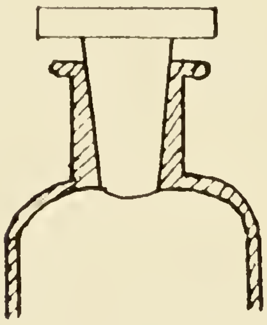

Fig. 84.

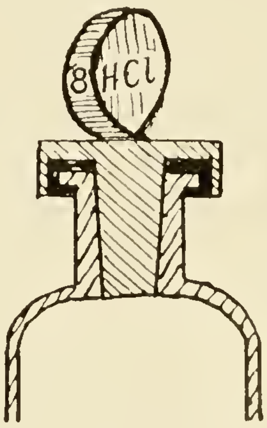

Fig. 85.

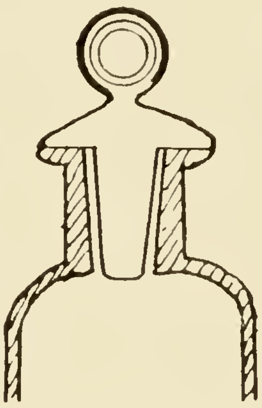

Fig. 86.

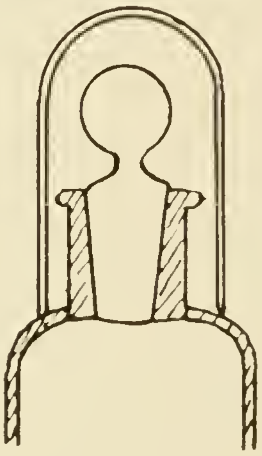

Fig. 87.

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[1] W. A. Dixon, *Chem. News*, **55**. 228, 1887 ; *ib.*, **78**. 294, 1898.

[2] Loosening Fixed Glass Stoppers and Stopcocks.—Usually the stoppers are not ground to fit the bottles well enough to prevent the slow evaporation of volatile liquids like ether, chloroform, etc. The better the stopper is ground into the bottle, the more it is liable to "stick." When a stopper is fixed, it can sometimes be loosened by tapping with the handle of a pocket-knife, followed by a twisting wrench with the fingers or a pair of pliers with a cloth between the pliers and the glass. Too powerful a wrench will break the stopper. If the bottle still resists, warm the neck with a cloth wet with hot water, or better, slowly warm the bottle by turning the neck rapidly in a Bunsen's flame at intervals of about a minute. The temperature of the neck is thus slowly raised. The stopper can be given a tap and wrench immediately after the neck has passed through the flame. Too great or too sudden heating will fracture the bottle. An obstinate stopper can sometimes be removed by leaving a little oil or glycerine above round the neck of the bottle, say overnight. A tap and wrench may then loosen the stopper. If the stopper be still fast, invert the bottle in a vessel of water so that the water reaches to the shoulder of the bottle. Let the bottle be inclined so as to prevent a bubble of air being entrapped in the gutter between the stopper and the bottle. This would prevent the water gradually working its way between the stopper and the bottle. The stopper may be tried with the tap and wrench after standing one, two, three, or four days. If it still resists, warm the water. As the water is warming, the bottle may be removed every now and again, to find if the stopper will yield to the tap and wrench. Time and patience are generally effective. Sometimes the bottle is wanted at once, and the tapping and wrench, or the heating over the Bunsen's burner, are continued until either the stopper loosens or the bottle breaks. The means taken to prevent accidents will naturally depend on the contents of the bottle. The naked flame would not be tried with a bottle of ether, nor would such a bottle be heated very much.

Swarts[1] has designed a glass stopper (fig. 86) which has the advantage of not sticking with solutions of caustic alkali, etc. The cone of the stopper fits the neck of the bottle loosely, but the flat part of the stopper on the under side, as well as the corresponding neck of the bottle, are polished flat, so that a close joint is obtained. These bottles cost about 25 per cent. more than ordinary stoppered bottles.

I prefer to keep the regular reagents in 250- and 500-c.c. resistance or Jena glass bottles with stoppers shaped as indicated in fig. 87, and with a rubber or loose glass cap placed over the neck as illustrated in the diagram. The 250-c.c. bottles (10s. 9d., unlabelled, per dozen) are recommended when only small quantities of solution are needed; the 500-c.c. bottles cost 13s. 6d. per dozen. The caps cost 1s. per dozen. When the bottles are in use, the stoppers can either be placed on a watch-glass or similar surface, or held between the fingers, or gripped in the palm of the hand, in such a manner as not to interfere with the using of the bottle for pouring, etc. For standard solutions 1000- or 2000-c.c. bottles are recommended (16s. 3d. and 23s. per dozen). Winchester bottles are usually excellent for this purpose, and are much cheaper.

The acid bottles, if convenient, are best kept on sheets of glass or rubber which rest on wooden shelves.[2] The labels of the acid bottles should be sand-blasted (4s. per dozen) or enamelled (6s. per dozen).

Books (1s.) of printed labels of the more common reagents are sold by the dealers. Special paper labels for solutions, made up according to the equivalent system described below, are available where enamelled or sand-blasted labels are not used. Blank labels are sold in packets and gummed ready for use.[3] The proper designation should be written in Indian ink. When the ink is dry, the label is gummed to the bottle and then coated with size.[4] When the size is dry, the whole is varnished [5]—one or two coats. Solids and liquids are usually supplied in corked or stoppered bottles. Their labels should be sized and varnished, as indicated above, before the bottles are shelved. Otherwise a bottle may be found with a label missing at an inconvenient time. Unprotected labels have a way of dropping off, and the writing is liable to fade in humid climates.

When an analysis—qualitative or quantitative—is in progress, the beakers, basins, flasks, and funnels should be labelled without delay. This will prevent confusing filtrates, precipitates, and samples with one another. A circular or oval patch can be sand-blasted on glass beakers, etc., so that they can be easily marked with a lead pencil. Faber manufactures a pencil (No. 2251) which can be used for writing (blue) on glass and porcelain.[6] It writes best if the surface is clean and warm. The writing can be removed by wiping with a damp cloth.

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[1] T. Swarts, *Chem. Ztg.*, 14. 836, 1890; A. Gawalovski, *Rundshau*, 1131, 1890; *Oel-Fett-Industrie*, 9. 114, 1892.

[2] Painting the side of the lip of the bottle—not the top of the bottle—with melted paraffin prevents solutions trickling down the outside, and incidentally facilitates the delivery of the reagent in drops—*Chem. News*, 65. 179, 1892.

[3] CEMENT FOR FIXING PAPER TO WOOD, GLASS, OR METAL.—Either of the following mixtures may be used:—(1) Dissolve 40 grms. of gum arabic and 10 grms. of gum tragacanth in 200 c.c. of water. Strain the solution through linen, and add 40 grms. of glycerine. Make the solution up to 400 c.c., and stir in 30 drops of oil of cloves to prevent putrefaction. (2) Rub 40 grms. of rye flour with 5 grms. of alum to a paste with 80 c.c. of water. Mix this with 200 c.c. of boiling water, and heat the solution until the paste is stiff when cold. Stir in 10 grms. of glycerine and 30 drops of oil of cloves.

[4] PAPER SIZE.—This can be made from isinglass or gelatine, or purchased from the dealers.

[5] PAPER VARNISH.—Quick-drying "paper" or "copal" varnish, from dealers in artists' materials, gives good results — the copal varnish for preference. If the size or varnish be unsuitable, or if the label has been imperfectly sized, unsightly greasy-looking patches will appear on the label. The first coat of varnish must be "set hard" before the second is applied.

[6] "Vitro ink" is sometimes useful for writing on glass. The writing will resist damp atmospheres and concentrated acids, but not boiling water or alkalies.

§ 74. The Action of Reagents on Glass and Porcelain.

In his study of the alleged transformation of water into earth, Lavoisier[1] (1770) showed that water dissolves glass vessels. This subject is of great importance in analytical chemistry. Errors may arise owing to the action of the acid on the glaze of the porcelain basins during the silica evaporation, etc., and some glazes are more readily attacked than others. Even the best of dishes are much eroded after they have been in use some time. Some of the poorer types of porcelain may lose 0·005 grm. in weight after a four-hours' evaporation of the hydrochloric acid solution, while the better types will not lose 0·0005 grm. by a similar treatment. The former number means that in a clay analysis with two evaporations, in that type of porcelain, the silica precipitate may be augmented 0·006 grm., the alumina precipitate 0·002 grm., and the lime precipitate 0·0003 grm. This matter therefore requires some attention. Of course the difficulty is overcome by evaporating in platinum basins, but that involves an outlay of over £20. It is therefore necessary under ordinary circumstances to use porcelain glazed with a resistant glaze.

The action of different solutions on glass is far more vigorous than on porcelain, but some types of glass resist better than porcelain with an unsuitable glaze. It is therefore bad, on principle, to allow filtrates, etc., to lie any length of time in porcelain or glass vessels—particularly the latter. In some cases the contamination from the glass may be serious. Thus, if glass contains arsenic[2] (page 285), an error may arise in toxicological work with serious consequences. A great many investigations have been made on the action of water and various solutions on glass and porcelain vessels.[3] The following may be taken to represent the amount in milligrams dissolved by 100 c.c. of the given reagents in four hours:—

Table XXIII.—Action of Reagents on Porcelain and Glass.

	Water.	HCl (20 per cent.).	H_2SO_4 (24 per cent.).	KOH (1 per cent.).	Na_2CO_3 (6 per cent.).
Berlin porcelain evap. basin .	0	0·06	0	5·6	3·3
German porcelain evap. basin	1·8	0·4	0·6	11	9·2
Bohemian glass flask . .	1·8	0·1	0·6	1·2	1·75
Common glass flask . .	1·4	2·7	8·0	5·3	4·8

From Cowper's work it appears that solutions of ammonium chloride and of ammonium sulphide usually attack glass rather more vigorously than sodium carbonate. It is important to bear these facts in mind when precipitations are made in ammonium sulphide solutions and left for some time, as is often done, to ensure the complete precipitation of the sulphides

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[1] A. L. Lavoisier, *Œuvres*, Paris, **2.** 1, 1864.

[2] W. Fresenius, *Zeit. anal. Chem.*, **22.** 397, 1883 ; S. R. Scholes, *Journ. Ind. Eng. Chem.*, **4.** 16, 1912.

[3] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2.** 767, 1905 ; Eng. trans., London, **2.** 626, 1900 ; A. Emmerling, *Liebig's Ann.*, **150.** 257, 1869 ; R. Weber and E. Sauer, *Zeit. angew. Chem.*, **4.** 662, 1891 ; *Ber.*, **25.** 70, 1814, 1892 ; F. Foerster, *ib.*, **22.** 1092, 1889 ; **25.** 2494, 1892 ; F. Mylius and F. Foerster, *ib.*, **22.** 1092, 1889 ; **24.** 1482, 1891 ; *Zeit. anal. Chem.*, **31.** 141, 1892 ; F. Foerster, *ib.*, **33.** 299, 322, 1894 ; C. Bunge, *ib.*, **52.** 15, 1913 ; P. Truchot, *Compt. Rend.*, **78.** 1022, 1874 ; R. Cowper, *Journ. Chem. Soc.*, **41.** 254, 1882. For a lengthy discussion on this subject, see H. Hovestadt, *Jena Glass*, London, 319, 1902. For toughened glass, see R. J. Friswell, *Chem. News*, **52.** 5, 1885 ; J. S. Stas, *ib.*, **17.** 1, 1868 ; F. Siemens, *Journ. Soc. Arts*, **33.** 386, 1885.

Mylius and Foerster give the following data for the action of water, 2N-NaOH and N-H_2SO_4 solutions at 100° for six hours., and a 2N-Na_2CO_3 solution at 100° for three hours. The numbers represent milligrams per square decimetre.

Table XXIV.—Action of Reagents on the Best Types of Glass Apparatus.

Type of Glass.	Beakers.					Flasks.				
	Water.		H_2SO_4.	NaOH.	Na_2CO_3.	Water.		H_2SO_4.	NaOH.	Na_2CO_3.
	20°.	80°.				20°.	80°.			
"R" .	0·0054	0·0144	0	41	23	0·0128	0·0128	0	51	26
Jena .	0·0071	0·0035	0	53	19	0·0063	0·0057	0	63	24
Bohemian	0·118	0·219	5	37	49	0·093	0·255	11	52	70

We are thus in a position to form some idea of what is taking place when filtrates, etc., are allowed to stand any length of time in porcelain or glass vessels. To illustrate the possible constituents to be found in the product of the reaction between the reagents and different types of glass, the following analyses are quoted from Walker's investigation[1] on chemical glassware :—

Table XXV.—Composition of Chemical Glassware.

Trade Name.	SiO_2.	Al_2O_3 and Fe_2O_3.	MnO.	ZnO.	MgO.	CaO.	K_2O.	Na_2O.	B_2O_3.	As_2O_3.
J. Kavalier's Bohemian .	76·02	0·64	tr.	...	0·30	7·38	7·70	7·60	...	...
Resistance "R" . .	68·00	2·32	0·14	2·40	5·04	4·80	1·82	10·17	5·53	0·24
"Wiener Normal Geräthe Glas"	74·00	0·66	0·01	0·24	0·16	7·76	5·51	9·69	2·15	...
Thüringen . . .	74·36	0·90	tr.	...	0·16	9·40	0·14	14·83	...	...
"Schott & Gen., Jena" .	66·74	2·77	0·65	8·28	4·50	0·28	0·08	8·99	7·18	...
"Nonsol W.T. Co." .	65·04	3·78	0·04	8·88	1·44	1·75	0·08	12·72	6·23	...
Bohemian . . .	70·80	1·00	1·04	...	0·08	7·88	7·67	8·59	...	...

The glaze of porcelain basins contains silica, alumina, alkalies, and alkaline earths. The glaze is of a felspathic type, with or without lime. In work with silicates, therefore, the best type of glass to use is obvious. It is unfortunate that the impurities introduced from the glass and porcelain vessels are those very constituents which have to be specially determined.

A few rules may now be indicated :—(1) If possible, do not allow the solutions to stand in glass or porcelain vessels for any length of time, particularly in glass. (2) If the work be interrupted, so that solutions must stand over, if there be no other objections, acidify the alkaline solutions before they are placed on one side. (3) If solutions must stand over, it is better to use good porcelain than glass vessels. (4) One of the three types of glass indicated in Table XXIV., or some other resisting glass, should be employed for general work in place of the more soluble types of glass. (5) For exact work, a blank experiment should be made, using nothing but the regulation reagents, in similar quantities, and under similar conditions to those actually employed in the analysis proper. This plan not only corrects impurities in the reagents, but it also enables us to practically eliminate the sources of error now under discussion. This has been done in the example given on page 185. (6) Precipitations made in alkaline solutions which have stood some time in glass vessels are almost certain to be contaminated with silica, and in exact work a correction must be made—*e.g.*, cobalt and nickel precipitations, page 391. (7) Remember that solutions of reagents are usually kept in glass vessels. Such solutions may accordingly be contaminated with silica, etc. See, for instance, the determination of phosphorus by the colorimetric process, page 603.[1]

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[1] R. H. Walker, *Journ. Amer. Chem. Soc.*, **27**. 865, 1905.

§ 75. The Equivalent System of making Solutions.

There are many advantages in making the concentrations of the liquids and solutions used in analytical work follow a definite system. Some make the solutions, as nearly as possible, on the "1, 2, 5, 10, 20, . . . parts of reagent per 100 parts of water" system. Wollny[2] recommends using multiples or submultiples of the equivalent weight (page 45) employed in volumetric analysis, but the solutions need not be made up with such a degree of accuracy as obtains in volumetric analysis. Hence, the amount of reagent in a given volume of solution is approximately known, and equal volumes of the reagents bear a fixed relation one to another. For instance, barium chloride (molecular weight 244) will have 122 grms. per litre. This is called an "E" solution; concentrated hydrochloric acid (molecular weight 36·5), of specific gravity 1·1565, has 365 grms. per litre, and is therefore a "10E" solution; potassium chromate (molecular weight 194·5) has 486 grms. per litre, and is therefore a "5E" solution. The same system was suggested by Reddrop in 1890. Reddrop (1890) recommended the designation "E," and Wollny (1885) the German equivalent "Aeq." The difference between an "E" solution and a "N" solution rests on the fact that a "normal" solution is supposed to be exact; the "equivalent" solution is approximate, and "rounded" atomic weights may be used in the calculations.

With this system, the amount of reagent required for a specific purpose can be readily calculated, and the addition of a great excess avoided. This means a saving in time, labour, and material; and it indirectly leads to more accurate and reliable work. Thus, 1 c.c. of an "E" solution of sulphuric acid or any sulphate will very nearly suffice for the quantitative precipitation of the barium from 1 c.c. of an "E" solution of barium chloride. Again, suppose that 1 grm. of clay be fused with 7·5 grms. of sodium carbonate (molecular weight 106), and the cooled mass taken up with water and an excess of hydrochloric acid. Since 7·5 grms. of sodium carbonate correspond with a little less than one-seventh of an equivalent (53), the addition of 14·3 c.c. of 10 E-HCl will suffice to neutralise the sodium carbonate. Hence, say, 15 c.c. of the acid will be an excess. If the acid be evaporated down to dryness twice, in the regular manner, and taken up the second time with 2 c.c. of the 10E-HCl, it will be obvious that 2 c.c. of 10E-NH_3 will suffice for the neutralisation of the acid, and 3 c.c. will be an excess of ammonia. This example shows how easily we can learn just how we stand with the quantities of the reagents present in our solutions. Measuring cylinders are useful for delivering definite volumes of the "E" solutions.

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[1] Ammonia and many other solutions are best kept in cerasine bottles or bottles lined with cerasine (cerasine is a white wax prepared from ozokerite)—O. Schreiner and G. H. Failyer, *Bull. U.S. Dept. Agric.* (*Soils*), **31**. 20, 1906.

[2] R. Wollny, *Zeit. anal. Chem.*, **24**. 402, 1885; R. Blochmann, *Ber.*, **23**. 31, 1890; J. Reddrop, *Chem. News*, **61**. 245, 256, 1890.

Wollny recommends the use of pipette bottles (fig. 30),[1] by means of which definite volumes can be quickly measured. These bottles, however, are rather expensive (4s. 6d each), though they are handy for a few of the more common reagents.

The strengths of the acids and ammonia are easily obtained by means of the hydrometer and the tables in the Appendix. For example, take sulphuric acid. From Table LXXIV. and the hydrometer we find that an acid of specific gravity 1·84 has 1759 grms. of H_2SO_4 per litre. Taking 49 as the equivalent of H_2SO_4, it follows that this acid is $\frac{1}{49}$ of 1759 = 36E strength. Obviously, 1 : 1 acid requires 500 c.c. of the concentrated acid per litre. The litre of the cold solution thus corresponds with 18E acid. If 5E acid be needed, the solution must contain $5 \times 49 = 245$ grms. of H_2SO_4 per litre. If 1759 grms. of H_2SO_4 correspond with a litre of the stock acid, 245 grms. of H_2SO_4 will correspond with 139·3 c.c. of the concentrated acid. This must be made up to a litre. In further illustration :—

Table XXVI.—Strengths of Stock Acids and Ammonia.

Sulphuric acid, sp. gr. 1·84=36E.		Hydrochloric acid, sp. gr. 1·16=10E.		Nitric acid, sp. gr. 1·50=22·4E.		Ammonium hydroxide, sp. gr. 0·88=18E.	
E.	c.c. acid per litre.	E.	c.c. acid per litre.	E.	c.c. acid per litre.	E.	c.c. per litre.
20	555·6	...	...	...	...	...	...
10	277·8	10	1000	10	446·5	10	555·6
5	139·3	5	500	5	223·2	5	277·8
1	28·0	1	100	1	44·7	1	55·6

The concentrations of the reagents used in this work are indicated in the footnotes where the reagents are first mentioned. These can easily be located by reference to the Index.

§ 76. Gas Generators.

The arrangements for the supply of hydrogen sulphide in a laboratory naturally depend upon the quantity of gas to be used at one time ; the frequency with which the gas is wanted, etc. An enormous number of generators have been devised with the object of giving a continuous stream of gas for intermittent periods. Many of the artifices designed for supplying the hydrogen sulphide partake of the nature of toys. They are not suited for serious work.

Preparation of Small Quantities of Hydrogen Sulphide.—The old-fashioned "Kipp," still much in vogue (fig. 153[2]), has many advantages and many disadvantages. The parts are not replaceable, so that if one part be fractured, as not infrequently happens while recharging, a new "Kipp" must be purchased. The acid is not well agitated, so that when that portion of the acid which comes in contact with the ferrous sulphide has lost its activity, the reaction becomes sluggish, and that frequently at a most inconvenient time. The "Kipp" must then be recharged, even though the acid be not exhausted. Several modifications of the original "Kipp" have been devised to rectify some of these faults. Wartha's (fig. 138) and Friswell's (fig. 122) modifications are improvements, and either of these forms will be found preferable to the ordinary "Kipp."

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[1] R. Wollny, *l.c.* ; Warmbrunn und Quilitz, *Chem. Ztg.*, 17. 454, 1893.

[2] The surface of the glass "Kipp," photographed in fig. 153, is much corroded by hydrofluoric acid.

If a great amount of gas be not required I recommend one of these forms.[1] Their advantages over the plain "Kipp" are: (1) the freshest acid is brought in contact with the solid (zinc, ferrous sulphide, marble, etc.); (2) the emptying and refilling is simple; and (3) a great over-pressure is avoided.[2]

Preparation of Large Quantities of Hydrogen Sulphide.—I prefer an apparatus of the type of de Koninck's[3] when large quantities of hydrogen sulphide are wanted at frequent intervals. L. L. de Koninck's apparatus (modified) is shown in fig. 88. The bottle *A* (1 to 2 litres) has two tubes on opposite sides near the base. This bottle is filled with glass marbles to a height of about 2 cm. above the side tubes. The remainder of the bottle is filled with ferrous sulphide (lumps or preferably sticks). By means of glass tubing, rubber joints, and perforated rubber stoppers, the side tubes are connected with the two side necks of a three-necked Woulff's bottle *B* (about 4 litres). One tube passes to the bottom of the bottle, the other passes just through the stopper. This latter tube has a side branch by means of which it is connected, by rubber tubing, with a side tube blown on to a bottle *C* (1 to 2 litres). The bottle *A* is connected with a Muencke's[4] gas washer *D* containing water. A three-way Greiner-Friedrichs' stopcock[5] is sealed on to the gas washer, and connected, by means of a rubber joint, with a tube passing through a rubber stopper in one of the necks of a three-necked Woulff's bottle *F* (2 to 4 litres), which has a tubulure fitted with a stopcock *J* ground and clamped to the side neck of the tubulure. The middle neck of the Woulff's bottle is fitted with a stoppered funnel *I*, which is convenient when the bottle is to be filled with water. The other neck of the bottle is fitted with a trap G.[6] The tube *H* leading from the trap passes to the stink closet, where it is fitted with two to four stopcocks which supply the gas to test tubes[7]

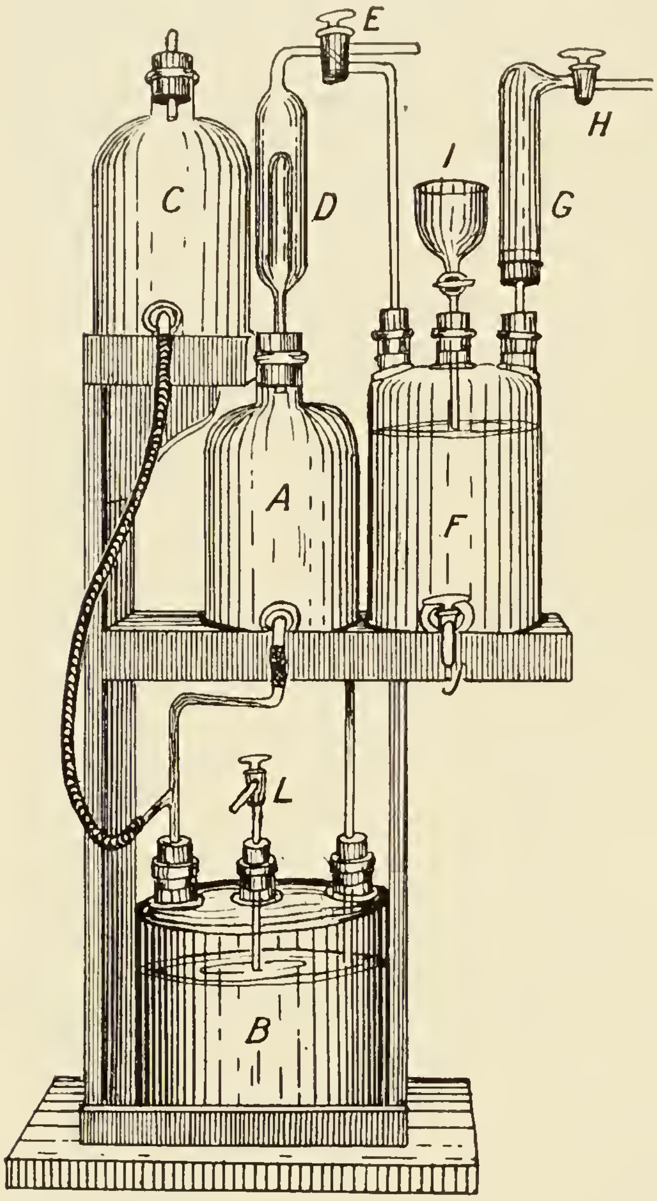

FIG. 88.—Hydrogen sulphide apparatus.

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[1] V. Wartha, *Ber.*, 151, 1872; *Zeit. anal. Chem.* **11**. 430, 1872; J. Meister, *ib.*, **25**. 373, 1886; R. J. Friswell, *Chem. News*, **90**. 154, 1904; **94**. 106, 1906; G. Thiele, *Chem. Ztg.*, **25**. 468, 1901; C. Arnold, *ib.*, **26**. 229, 1902.

[2] The drying and washing bottles can be fixed to the apparatus itself by suitable clamps—H. Reckleben, *Chem. Ztg.*, **35**. 279, 1911.

[3] L. L. de Koninck, *Chem. Ztg.*, **17**. 1099, 1893; *Journ. Amer. Chem. Soc.*, **16**. 63, 1894; F. M. Perkin, *Journ. Chem. Soc. Ind.*, **20**. 438, 1901. Perkin added the bottle for storing "H_2S water" and also improved the joints.

[4] R. Muencke, *Zeit. anal. Chem.*, **15**. 62, 1876.

[5] E. Greiner and Friedrichs, *Zeit. anal. Chem.*, **26**. 50, 1887.

[6] To prevent contamination by sucking back if, by accident, *H*, etc., be opened before *E*.

[7] Blocks of wood, 5 cm. thick, with a hole 4 cm. deep and 2 cm. diam., are useful for supporting test tubes while their contents are being subjected to the action of the gas. There are several ways of delivering the gas in the fume chamber—C. L. Parson, *Journ. Amer. Chem. Soc.*, **25**. 231, 1903.

or flasks. The free way to the tap *E* is convenient if a current of gas is to be led elsewhere, say, to an apparatus on a working bench.

All the rubber connections should be wired on to prevent leakage. The whole apparatus may be mounted on a wooden stand as shown in the diagram. The bottles should be prevented moving from their position by screwing three pieces of wood to their part of the wooden base. The middle neck of *B* has a perforated stopper fitted with a stoppered tube passing to the bottom of the bottle.

To charge the apparatus: open all the stopcocks, pour dilute hydrochloric acid[1] into *C*. When the acid has risen to *L*, close this cock. When the acid commences to rise in *A*, close *E*, and the other stopcocks. Pour the remainder of the acid into *C* until *C* is between half and three-fourths filled. Fill the bottle *F* with cold, recently boiled distilled water *viâ* the stoppered funnel *I*.[2] Connect *D* with *F* by means of the stopcock *E*, and the apparatus will be ready for use in a short time. The absence of all but a trace of air from the atmosphere in the bottle *F* when in use retards the decomposition of the solution in *F*, and only a trace of sulphur will be deposited in *F* by the oxidation of the "H_2S water."

To empty the apparatus for cleaning: connect the tube *L* with a rubber tube, open the stopcock, and the acid will soon be syphoned into a suitable receiver—say the sink. To recharge the apparatus: close the stopcock *L*, connect *E* with the atmosphere, and proceed as before to pour fresh acid into *C*. To introduce new ferrous sulphide: remove *D* by loosening the rubber joint and the rubber stopper.

Although this apparatus costs 45s., and a large-size "Kipp" 19s., it is worth the difference. (1) The acid and ferrous sulphide do their work more efficiently and economically; (2) when the apparatus is not in use it need not stand under pressure, for *C* can be lifted on to the base, and the cock *E* closed;[3] (3) the gas can be obtained under great pressure by using a longer connection for *C* and lifting *C* to a higher level; and (4) each part can be easily replaced, and the cost for breakage is very small.

Hydrogen Sulphide free from Arsenic.—In special work, toxicological investigations, etc., it is necessary to employ hydrogen sulphide quite free from arsenic. It is then necessary either to purify the gas by a suitable train of wash-bottles, etc.,[4] or to employ materials free from arsenic in the gas generator. The former is the more troublesome process; the latter is usually the most convenient. Various mixtures have been recommended for this purpose. Fresenius[5] used calcium sulphide in a "Kipp" with dilute hydrochloric acid (1 volume acid, sp. gr. 1·12; 1 volume water); Winkler[6] recommends barium sulphide; others,[7] mixtures of these two sulphides; Divers and Schimidzu[1] recommend magnesium sulphide; Hampe[2] uses sodium sulphide with dilute sulphuric acid (1 : 10); etc.[3] The sulphides here named are relatively easy to prepare free from arsenic.

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[1] Concentrated hydrochloric acid, 2 volumes, water 3 volumes. With bottles the sizes mentioned above, a Winchester of acid mixed with 1½ Winchesters of water will suffice for a charge. Sulphuric acid is objectionable because the ferrous sulphate is liable to crystallise and choke the tubes.

[2] Covered by a lid to keep out dust.

[3] Although *E* is usually left connecting *A* with *F*, and *C* as shown in the diagram, *E* must always be closed before *C* is lifted down, and *C* must be lifted, as shown in the diagram, before *E* is opened. Otherwise, water will flow from *F* to *A*. *C* can be corked when not in use, or it can be fitted with a perforated rubber stopper and tube leading into the stink closet or outside the building.

[4] O. von der Pfordten (*Ber.*, **17**. 2897, 1884) purifies the gas from ferrous sulphide and hydrochloric acid by passing it over a layer of potassium monosulphide at 300°–350°.

[5] R. Fresenius, *Zeit. anal. Chem.*, **26**. 339, 1887.

[6] C. Winkler, *Zeit. anal. Chem.*, **27**. 26, 1887.

[7] R. Otto and W. Reuss, *Archiv Pharm.* (3), **20**. 919, 1884; *Ber.*, **16**. 2947, 1883; H. Klosmann, *Ber.*, **17**. 209, 1884; B. Kosmann, *Chem. Ztg.*, **8**. 138, 1884; W. Lenz, *Zeit. anal. Chem.*, **22**. 393, 1883; H. Hager, *Pharm. Centr.* (2), **5**. 212, 1860.

Washing Carbon Dioxide.—See page 192.

Washing Hydrogen Gas.—One way of cleaning hydrogen is indicated on page 390; another, more thorough process, is to attach the following train to the automatic generator: (1) A saturated solution of mercuric chloride to remove hydrocarbons; (2) potassium hydroxide bulbs; (3) silver nitrate solution; (4) pieces of solid potassium hydroxide; (5) granulated calcium chloride. See also page 391.

Washing Air.—The air is forced or drawn through the following train: (1) Concentrated sulphuric acid; (2) concentrated potassium hydroxide; (3) concentrated sulphuric acid.

§ 77. Distilled Water.

The water used in quantitative analysis should be distilled from a tin-lined copper still connected with a tin-lined copper or a block-tin condenser.[4] The still is usually fitted with an automatic filler, so that the overflow water from the water jacket of the condenser can run into the still. When a supply of steam is available, the still can be replaced by a tin-lined copper cylinder. The cylinder is fitted with a couple of perforated shelves supporting layers of calcined quartz pebbles, which serve to filter the steam and prevent dirt being mechanically carried over to the condenser. In some cases the distilled water is obtained by affixing the condenser to the steam apparatus used for drying, heating, etc.[5] All depends upon the local conditions—the quantity of distilled water required per diem, etc. Stills of the type illustrated in fig. 89 are compact and convenient where but small quantities are needed. The still can be fixed to a wall in any convenient place. These stills are made of different sizes—capacity from 2 to 10 litres per hour; price from 50s.

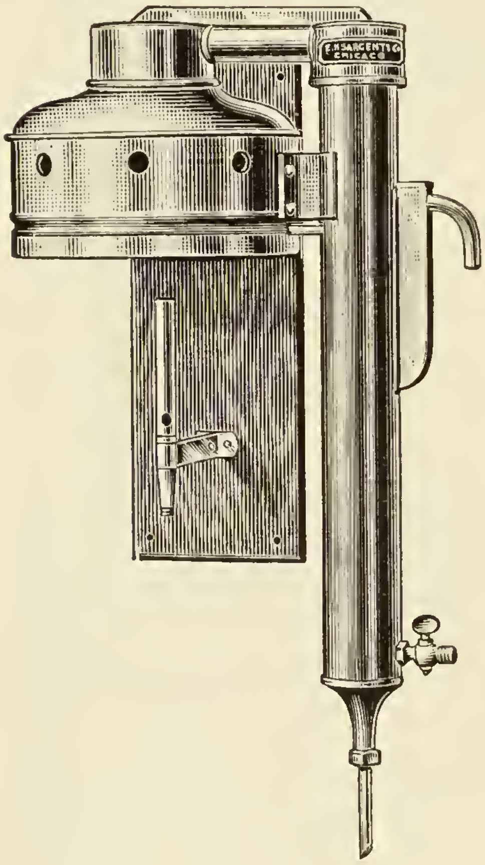

Fig. 89.—Jewell's water still.

If the water is to be freed from carbon dioxide and ammonium carbonate, the first portions which pass from the still (not an automatic still) are rejected, and the water should be boiled some time to drive off the adsorbed gases—air, carbon dioxide, etc. If the water is to be free from organic matter, it can be distilled from an alkaline solution of potassium permanganate. This, however, does not destroy all the ammonia. To remove the ammonia, Stas[1] distilled the water from aluminium sulphate.

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[1] E. Divers and T. Schimidzu, *Journ. Chem. Soc.*, 45. 270, 1884.

[2] W. Hampe, *Chem. Ztg.*, 14. 1777, 1890; F. Gerhard, *Archiv Pharm.* (3), 23. 384, 1885.

[3] J. Habermann (*Verhandl. naturf. Ver. Brünn*, 17. 14, 1891) heats a mixture of one part calcium sulphide with two parts of magnesium chloride and enough water to make the whole into a thin slurry.

[4] Distilled water is almost without action on block tin. Water condensed in glass tubes is objectionable because the water dissolves appreciable quantities of glass. This can be demonstrated (*a*) by evaporating such water to dryness in a platinum dish; and (*b*) by the fact that the glass tubes soon become deeply corroded.

[5] L. W. Hoffmann and R. W. Hochstetter, *Journ. Amer. Chem. Soc.*, 17. 122, 1895; C. E. Wait, *ib.*, 17. 917, 1895; H. M. Hall, *Journ. Anal. App. Chem.*, 6. 190, 1892; R. Seligman, *Chem. News*, 93. 27, 1906.

Receiver for Distilled Water.—The receiver for the distilled water depends upon the amount of water required per diem, etc. Owing to the fact that distilled water attacks glass, the water should not be kept any great length of time in glass vessels. Tanks linked and soldered with block tin are best for laboratories where inorganic gravimetric determinations are made, since the water is then free from silica, etc., which lead to high results. The tank can be fitted with a glass syphon gauge. Some use a couple of glass bottles with glass stopcocks at the side. One bottle is filled in the morning and used for the next day's supply. Each bottle is emptied the night after it has been filled with distilled water. The distilled water should be tested every now and again by evaporation in a weighed platinum dish to make sure that it is free from contaminations.

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[1] J. S. Stas, *Chem. News*, **4**. 207, 1861 ; **15**. 204, 1867 ; *Zeit. anal. Chem.*, **6**. 417, 1867 ; *Œuvres Complètes*, Bruxelles, **1**. 101, 536, 1894.

PART II.

TYPICAL SILICATE ANALYSES—CLAYS.

CHAPTER X

THE DETERMINATION OF VOLATILE MATTERS.

§ 78. Hygroscopic Moisture.

THE term "hygroscopic moisture" generally includes all the volatile constituents, principally moisture, which are given off when the substance is heated to a certain standard temperature, say, 110°.[1] The heating is continued until the substance ceases to lose weight. The ground[2] sample is placed in a stoppered weighing bottle of known weight. The bottle and contents are then weighed, and placed in an air bath[3] at the desired temperature. The stopper is removed, and a piece of filter paper is placed over the mouth of the weighing bottle to keep out the dust. The bottle and contents can be left in the oven overnight; the stopper of the weighing bottle is placed in the desiccator with the bottle; and, when cold, the stopper is inserted and the whole weighed. About four hours usually suffices for the drying, but, after weighing, the bottle is then returned to the air bath for an hour, and, when cold, re-weighed. If no further loss of weight occurs, the hygroscopic moisture of the clay in the bottle is represented by the total loss of weight which the clay suffers when dried at 109°–110°. The finely ground powder is dried in another stoppered bottle, in a similar manner, for subsequent analysis.

One purpose of removing the hygroscopic moisture before the analysis is to secure a uniform hygroscopic condition as a basis for comparing the analytical data.[4] If an analysis were made on two samples of one clay, one sample with 5 per cent. less hygroscopic moisture than the other, the silica in one might appear, in the statement of the analysis, as 60 per cent., and in the other as 57 per cent. This all in the same clay. Hence, the analytical results will appear different according as the sample is collected in moist or in dry weather.

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[1] Some heat the clay to 100°, but this is scarcely high enough; others use 105°, 120°, etc.

[2] Most finely ground powders absorb moisture so tenaciously that some is retained even after the powder has been heated to 110° an indefinitely long time. In fact, R. Bunsen (*Wied. Ann.*, **24**. 327, 1885; A. L. Day and E. T. Allen, *Amer. J. Science* (4), **19**. 93, 1905; J. T. Bottomley, *Chem. News*, **51**. 85, 1885) has shown that a red heat is required for the expulsion of all the adsorbed water.

[3] Either a toluene bath, fig. 90, or a bath fitted with a thermostat, fig. 116—both are shown with the door open. Instead of toluene, a mixture of water and glycerol may be used: 6 parts of water to 1 of glycerol boils nearly at 105°; and a mixture of 1 part of water to 6 parts of glycerol, at 120°. Intermediate temperatures can be obtained by the use of intermediate mixtures. If the proportion of glycerol be increased much beyond the limit here mentioned, acrid fumes are given off—E. J. Reynolds, *Chem. News*, **4**. 319, 1861. An aqueous solution of calcium chloride, which boils at the desired temperature, can also be used, *e.g.*, 100 grms. of water with 25 grms. of calcium chloride boils at 105°; with 41·5 grms. calcium chloride, at 110°; with 69 grms. of calcium chloride, at 120°—G. T. Gerlach, *Zeit. anal. Chem.*, **26**. 413, 1887. I prefer toluene. Concentrated solutions of calcium chloride sometimes cause trouble by attacking the joints of the bath, and require more attention owing to the gradual loss of water. To prevent any escape of inflammable toluene vapours into the room should the water of the condenser be turned off while the bath is going, say overnight, I have a tube (*a*, fig. 90) leading from the top of the condenser to the outside of the laboratory.

[4] See Z. A. James, *Eng. Min. Journ.*, **90**. 1047, 1910.

It is generally advisable, with commercial materials, to determine the amount of "hygroscopic moisture lost at 100°" or "at 110°."[1] For clays, it is best to use 109°-110°. Some materials would be decomposed at this temperature. For example, superphosphates are liable to decompose at 110°. This is illustrated by the following determinations of the weights of acid calcium phosphate[2]—$CaH_4(PO_4)_2$—when heated one hour at the temperatures stated :

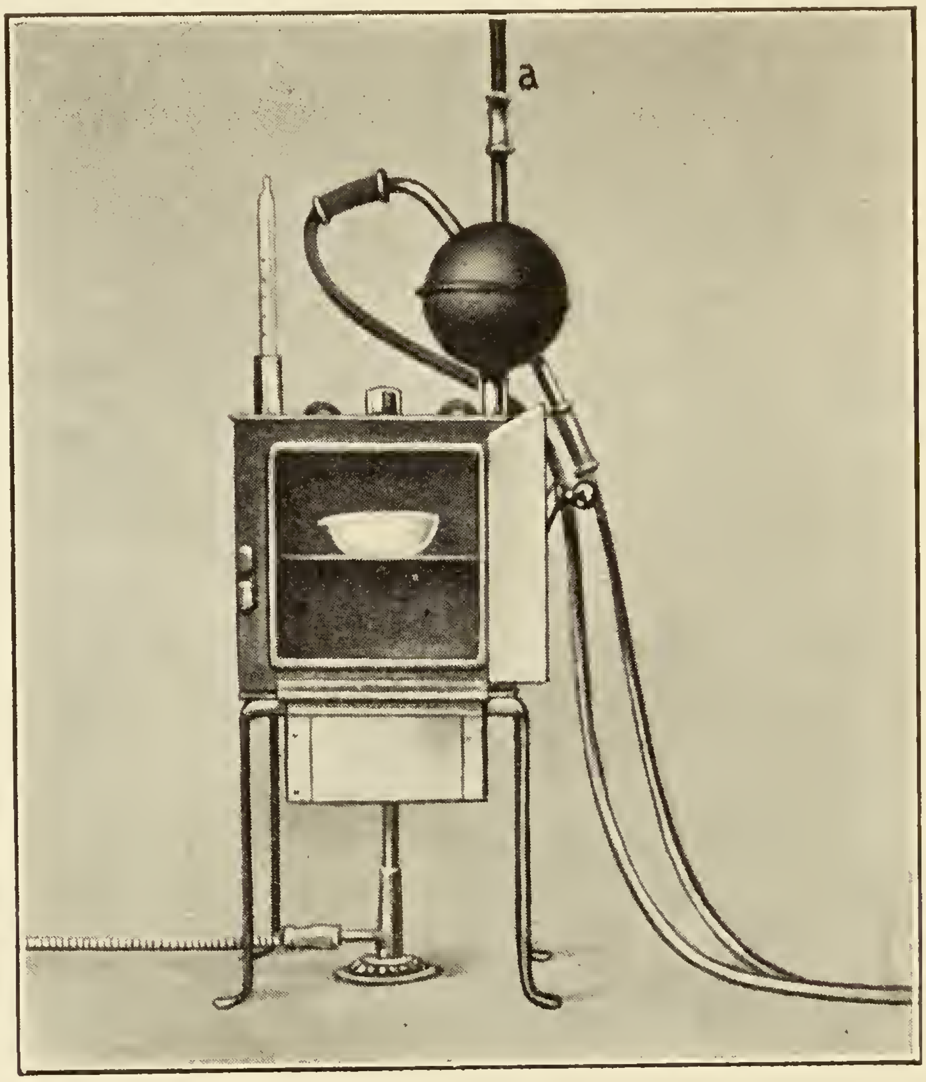

Fig. 90.—Toluene bath at 109°-110°.

Temperature . .	100°	105°	110°	120°	130°	140°	150°	160°	200°
Decomposition .	0	2·0	4·3	4·9	6·6	8·4	13·3	17·7	50·4 per cent.

If the samples for analysis are received in paper or in canvas bags, it is not much use determining the hygroscopic moisture, because the result may be greater or less than when the sample was originally packed for the analyst. If the hygroscopic moisture is to be determined, the sample should be hermetically sealed in a vessel which will not allow an absorption or evolution of moisture. There are some "tricks" in sampling when the moisture question is left open.[3]

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[1] For the moisture retained by many salts dried in a steam oven—97°-98°—see H. W. Hake, *Proc. Chem. Soc.*, **13**. 147, 1897 ; F. W. Smither, *Amer. Chem. Journ.*, **19**. 227, 1897. 0·2864 grm. of calcium chloride, $CaCl_2$, after the 30th day, weighed 0·3200 grm. ; 0·4349 grm. calcium nitrate, $Ca(NO_3)_2$, 0·4550 grm. ; 0·1907 grm. magnesium chloride, $MgCl_2$, 0·2136 grm. The numbers varied a little according to the hygroscopic condition of the atmosphere. Obviously, therefore, we cannot consider drying in the steam oven, and possibly air baths, a sufficient means of standardising the hygroscopic condition of all materials.

[2] J. Stoklasa, *Zeit. anal. Chem.*, **29**. 390, 1890 : H. Birnbaum, *Zeit. Chem.* (2), **14**. 137, 1871. For white lead, see p. 319.

[3] Spooner and Bailey, *Chem. News*, **21**. 21, 1870.

In order to distinguish between the moisture which has been absorbed by a given substance from its surroundings, and that which is given off by the decomposition of hydrated aluminium silicates, salts with water of crystallisation, etc., at 110°, the substance is dried, not at 110°, in an air bath, but at atmospheric temperatures in a desiccator over concentrated sulphuric acid—preferably *in vacuo*. This may occupy days or even weeks. The time can be shortened by drying the powder in a tube, in a current of air, dried by passage through, say, sulphuric acid, followed by phosphorus pentoxide. The loss in weight indicates the amount of moisture lost.[1] The moisture can be reabsorbed in a drying tube charged with phosphorus pentoxide, and the increase in its weight represents the moisture removed from the clay. This gives the hygroscopic moisture less the trace which the clay retains with remarkable tenacity, even at elevated temperatures.

The atmosphere in some air baths, steam ovens, etc., is quite humid, and contaminated with sulphurous oxides, etc., arising from the products of the combustion of the coal gas beneath the oven. These gases find their way into the oven between the door and the front of the oven. In the diagrams, figs. 90 and 116, these gases are shown deflected up the back of the oven, where they do no harm. A ledge vertically downwards is fixed on the front and on two sides, as shown in the diagrams. There are also certain risks attending the use of ovens lined inside with metal. Dust from the corroded metal may fall on to the materials being dried. It is not difficult to line an oven with glazed porcelain or earthenware slabs, which can be obtained to fit the oven.[2]

§ 79. Loss on Ignition.

This term is employed to represent the total loss in weight which occurs when the clay is calcined at a bright red heat. The "loss on ignition" may thus include the loss in weight which attends the expulsion of water (page 573) formed during the decomposition of the clay; carbon dioxide from the carbonates (page 553), sulphurous gases from the sulphates, and the oxidation of sulphides;[3] the combustion of carbon and organic matter (page 546); the volatilisation of ammonium compounds, alkalies, etc. The loss in weight on ignition is usually great enough to mask the gain in weight which occurs during the more or less incomplete oxidation of ferrous to ferric and magnetic oxides; manganese compounds to Mn_3O_4, etc. However, it is not uncommon to find firebricks which *gain* up to 0·5 or even 1·0 per cent. on ignition. This is probably due to the oxidation of ferrous and metallic iron. Sometimes these bricks, when powdered and treated with acids—dilute hydrochloric acid, for instance—give off hydrogen gas, showing the presence of metallic iron.[4] The loss on ignition is not always satisfactory for exact investigations,[5] but for industrial purposes it sometimes indicates what is likely to happen when a clay is fired in the ovens or kilns.

To determine the loss on ignition, about 1 grm.[6] of the clay is calcined in a weighed platinum crucible recently heated red-hot, and cooled in a desiccator. The crucible, during the earlier stages of the ignition, is inclined 30°–45° on a platinum or quartz triangle, as indicated in fig. 91. The flame is so arranged that it does not envelop the whole crucible, but impinges on one side, so that the air can circulate freely about the mouth of the crucible. Some clays, ball clays in particular, must be heated very slowly at first, or fine particles of clay will be carried away from the crucible with currents of gas and steam. A blast is usually needed for the later stages of the ignition.[1] A crucible is shown in fig. 92 being heated over a blast. After the clay has been blasted about 10 minutes, the crucible is allowed to cool until down to a temperature below red heat. It is then lifted into the desiccator by means of a pair of platinum-pointed tongs, allowed to cool, and weighed. Again blast the crucible and contents 5 minutes, cool, and weigh as before. If a further loss in weight takes place, the blasting must be repeated until two successive weighings are approximately constant.

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[1] When this experiment is done carefully, some very curious curves are obtained. Part of the water, usually thought to be "combined water," behaves as if it were "hygroscopic moisture"—E. Löwenstein, *Zeit. anorg. Chem.*, **63**. 69. 1909. See page 575.

[2] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 21, 1911; Eng. trans., 22, 1904.

[3] The sulphur may be retained by free lime, etc., if present in the form of sulphates.

[4] F. Stolba (*Zeit. anal. Chem.*, **7**. 93, 1868) shows that a correction can be made if the amount of ferrous oxide be determined, because one part of this oxide increases by 0·1111 grm. on passing to the ferric condition.

[5] For the direct determination of water, carbon, carbon dioxide, etc., see later chapters.

[6] If the clay be not very hygroscopic, exactly 1 grm. may be weighed out. This saves trouble in calculations, but it is necessary to guard against the error mentioned on page 54.

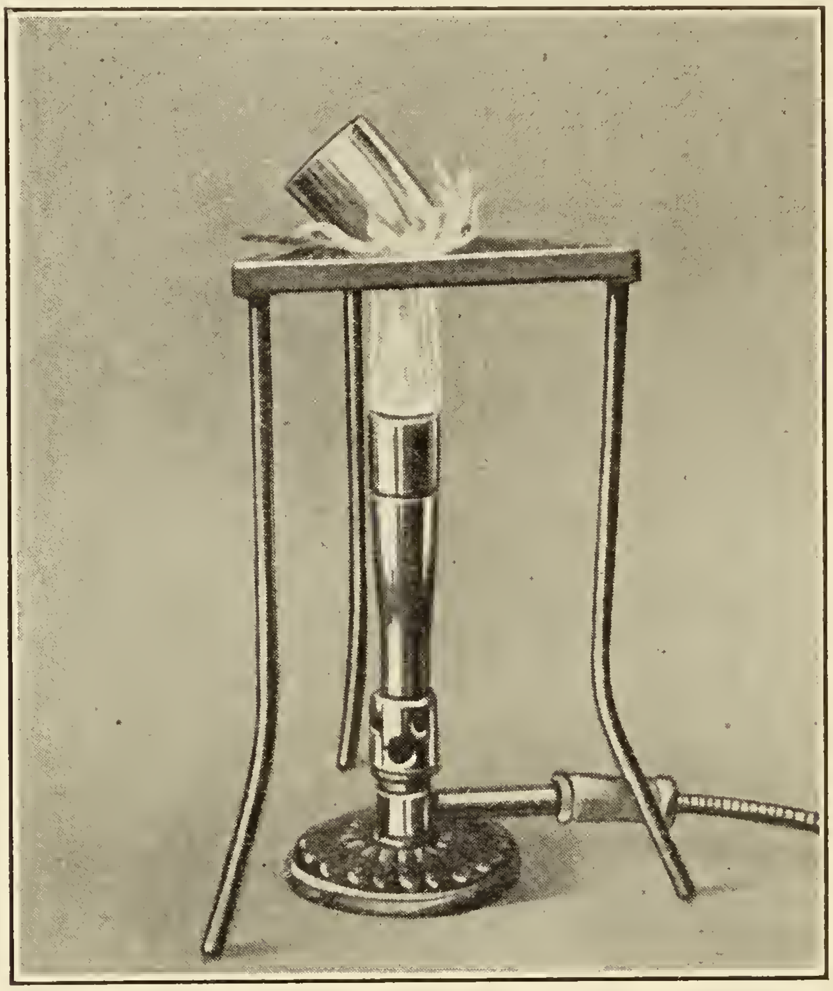

Fig. 91.—Ignition over a Méker's burner.

Highly carbonaceous clays are sometimes advantageously mixed with a known weight of ignited magnesia to prevent the fusion or agglomeration of the residue during ignition.[2]

Errors.—Determinations of the loss on ignition of eight portions of one sample of powdered clay, each weighing 1 grm., gave the following numbers:—0·0927, 0·0933, 0·0927, 0·0931, 0·0931, 0·0930, 0·0929, 0·0930 grm., with a mean of 0·0930 grm., that is, 9·30 per cent., with a maximum and minimum deviation of ± 0·03. These numbers give us an idea of the differences which might be expected in duplicate determinations. If another analyst made a determination, his result ought not to differ by much more than ± 0·03 from the 9·30 per cent. If it did, one of the results is wrong, or the sampling is faulty, or the "drying temperature" is different from 110°.

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[1] Alkalies begin to escape at a red heat. Potassium usually comes off faster than sodium. The alkalies, after a long blasting, may be found partly condensed on the lid. If the blasting be long continued, most of the alkalies will be volatilised in this way. If the ignition temperature be properly adjusted, the loss of sulphur and alkalies is inappreciable.

[2] According to A. Gutbier (*Chem. Ztg.*, 34. 211, 1910), W. C. Heraeus has designed a perforated crucible lid with a partition extending into the crucible. By heating one side of the crucible a circulation of air is induced which is said to facilitate the combustion of organic matter.

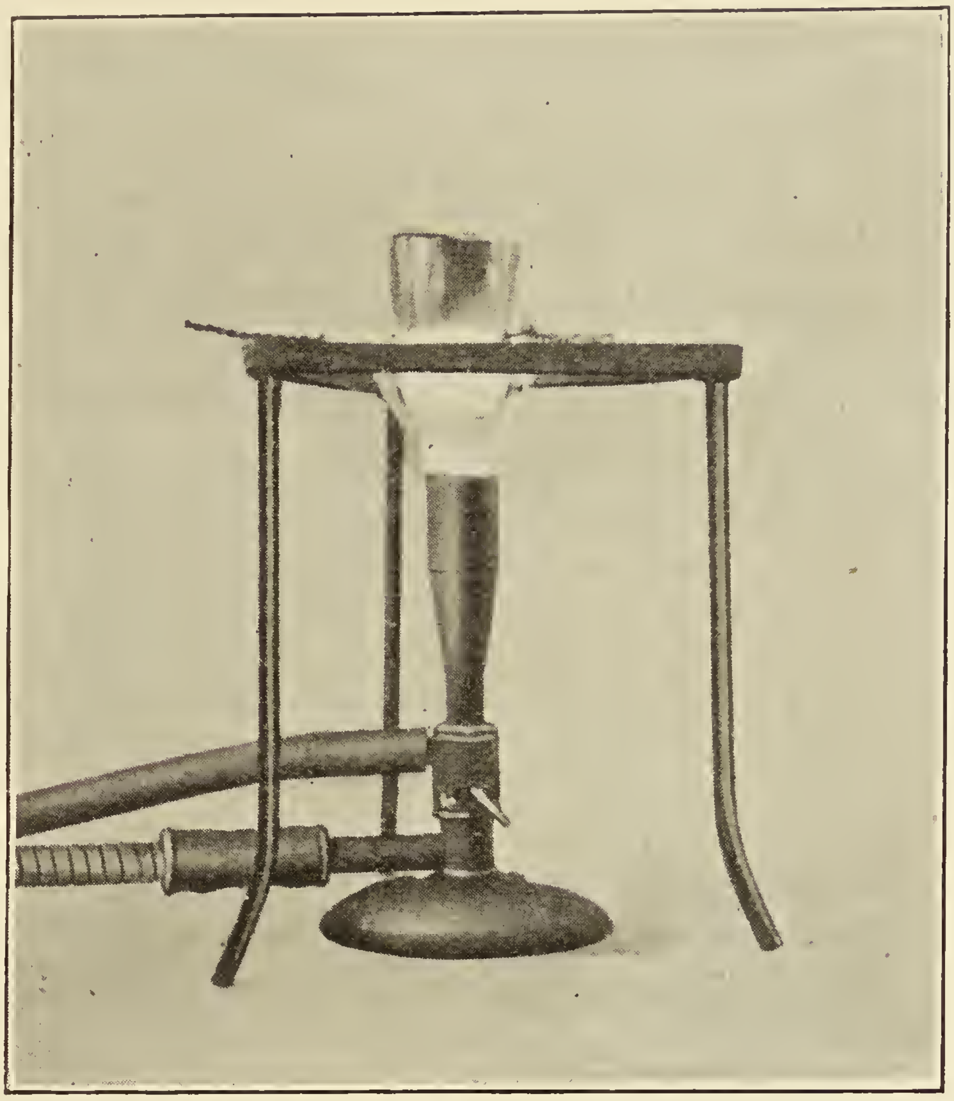

FIG. 92.—Ignition over a blast Méker's burner.

The chief sources of error arise from: (1) Imperfect drying (hygroscopic moisture); (2) Oxidation or reduction of ferrous iron, etc.; (3) Imperfect expulsion of water owing to a too low temperature of ignition;[1] (4) More or less imperfect decomposition or volatilisation of some of the constituents—fluorides,[2] sulphates,[3] etc.; and (5) Mechanical loss of the substance by the transport of fine particles along with the steam when the temperature is raised too rapidly.[4]

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[1] Some minerals—*e.g.* talc, steatite, etc.—require a high blasting temperature to drive off all the water.—T. Schurer, *Pogg. Ann.*, 84. 321, 1851.

[2] K. List, *Liebig's Ann.*, 81. 189, 1852.

[3] C. R. Fresenius (*Quantitative Chemical Analysis*, London, 1. 55, 1876) says the loss of sulphuric acid from sulphates can often be guarded against by adding about six times the weight of the substances of finely divided, recently ignited lead monoxide.

[4] G. Cesaro, *Mém. Soc. Roy. Sciences Lièges* (3), 5. 1, 1906.

CHAPTER XI.

OPENING UP SILICATES.

§ 80. Summary of the Different Methods.

Some silicates are easily decomposed by more or less prolonged digestion in acids; others require a more drastic treatment. Some, apparently insoluble silicates, decompose in acids after a preliminary calcination at 500°-600°. A great variety of methods have been proposed and used.[1] Many of these methods are now obsolete. Although the sodium carbonate fusion is generally employed, some of the other methods are invaluable in special cases. A number of methods are indicated below; others will be described later in connection with glazes and glasses, also chromite and uranium.

I. *Silicates decomposed by Digestion with Mineral Acids.*—Sulphuric, hydrochloric, or nitric acid, or mixtures of these acids—in open vessels.

(*a*) Natural silicates. Used for the so-called "rational analysis"; analysis of slags, some lead frits, etc. See pages 460, 657 *et seq.*

(*b*) After the silicate has been calcined at a dull red heat, below the melting point of the silicate.[2] *E.g.*, tourmaline in hydrofluoric acid, etc. See page 460.

(*c*) After exposure to reducing gases at a dull red heat. See page 269.

(*d*) Digestion with hydrochloric or sulphuric acids in sealed tubes, under pressure.[3] See page 493.

II. *Silicates decomposed by Hydrofluoric Acid alone or by a Fluoride mixed with a Mineral Acid.*—Sulphuric, hydrochloric, or nitric acid.

(*a*) Vapour at a red heat.[4]

(*b*) Aqueous solution alone or with mineral acids.[5] This process is much used for the determination of ferrous iron and alkalies, etc.

(*c*) Digestion with a fluoride mixed with an acid or some salt which decomposes the fluoride.

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[1] For the decomposition of chromite, see page 474; and for ferruginous minerals, page 461.

[2] F. Mohr, *Zeit. anal. Chem*, **7**. 293, 1868; F. Rocholl, *ib.*, **20**. 289, 1881; C. Rammelsberg, *Pogg. Ann.*, **80**. 457, 1850; H. Rose, *ib.*, **108**. 1, 1859; see page 461, FeO.

[3] A. Mitscherlich, *Journ. prakt. Chem.* (1), **81**. 108, 1860; **83**. 455, 1861; P. Jannasch, *Ber.*, **24**. 2734, 3206, 1891; *Zeit. anorg. Chem.*, **6**. 72, 1894; F. C. Phillips, *Zeit. anal. Chem.*, **12**. 189, 1873.

[4] A. Brunner, *Pogg Ann.*, **44**. 134, 1838; F. Kuhlmann, *Compt. Rend*, **58**. 545, 1864; A. H. Allen, *Analyst*, **21**. 87, 1896; A. Müller, *Journ. prakt. Chem.* (1), **95**. 51, 1865.

[5] J. J. Berzelius, *Pogg. Ann.*, **1**. 169, 1824; H. Rose, *Liebig's Ann.*, **72**. 324, 1849; D. Craig, *Chem. News*, **60**. 227, 1889; E. Linnemann, *ib.*, **52**. 220, 233, 240, 1885; N. S. Maskelyne, *ib.*, **21**. 27, 1870; *Proc. Roy. Soc.*, **18**. 147, 1869; F. Hinden, *Zeit. anal. Chem.*, **25**. 332, 1906.

(i) Ammonium fluoride and sulphuric acid.[1]
(ii) Potassium hydrogen fluoride.[2]
(iii) Calcium fluoride and sulphuric acid.[3]
(iv) Sodium fluoride with an acid or with potassium bisulphate.[4]
(v) Barium fluoride with an acid or with barium nitrate.[5]

III. *Silicates decomposed by Fusion with Alkaline Oxides or Salts.*—This method is not usually applied if the silicate is decomposed by simple treatment with acids, in open vessels.

(*a*) Fusion with alkaline hydroxides. Fused caustic potash and soda ash were among the earliest fluxes in use for decomposing silicates.[6] Pure sodium carbonate and caustic soda are now much used for opening up silicates.[7]

(*b*) Fusion with sodium peroxide. This is much used for opening up chromites hæmatites, etc., as described on pages 266, 461, etc. The violence of the action may be tempered by mixing the peroxide with sodium hydroxide or lime.

(*c*) Fusion with alkaline carbonates.
(i) Sodium carbonate.[8]
(ii) Fusion mixture.[9]
(iii) Sodium bicarbonate.[10]
(iv) Potassium carbonate.[11] This salt is sometimes preferred to sodium carbonate—*e.g.*, with tungstates, niobates, tantalates, etc.—on account of the greater solubility of the potassium salt.

(*d*) Potassium or sodium bisulphate or pyrosulphate.[12] Smith prefers the sodium salt in certain cases—*e.g.*, in the decomposition of corundum—since the double salt of aluminium and potassium is dissolved with greater difficulty under conditions where the sodium salt is freely soluble.

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[1] L. von Babo, *Amt. Ber. deut. Naturforscher. Aertze Mainz*, **20**. 103, 1842 ; J. Potyka, *Untersuchungen über einige Mineralien*, Berlin, 38, 1859 ; H. Rose, *Pogg. Ann.*, **108**. 20, 1859 ; R. Hoffmann, *Zeit. anal. Chem.*, **6**. 367, 1867 ; *Chem. News*, **17**. 24, 1868. The ammonium fluoride should leave no residue when evaporated to dryness. P. T. Austen and F. Wilber (*Chem. News*, **48**. 274, 1883) purify by dissolving commercial ammonium fluoride in as little water as possible in a platinum dish (or, better, place hydrofluoric acid in a platinum dish), add an excess of concentrated ammonia slowly from a pipette to avoid loss by spurting. A voluminous precipitate may separate. Decant the clear liquid for use. In silicate decompositions, acidify the solution with sulphuric acid and evaporate to dryness.

[2] C. Marignac, *Ann. Chim. Phys.* (4), **8**. 115, 1866 ; W. Gibbs, *Amer. J. Science* (2), **37**. 357, 1864 ; *Chem. News*, **10**. 37, 49, 1864 ; F. A. Clarke, *Zeit. anal. Chem.*, **7**. 463, 1868.

[3] C. E. Avery, *Chem. News*, **19**. 270, 1860 ; C. A. Wilbur and W. Whittlesey, *ib.*, **22**. 2, 1870.

[4] F. W. Clarke, *Amer. J. Science* (2), **45**. 173, 1868 ; (3), **18**. 290, 1877 ; *Chem. News*, **17**. 232, 1868 ; C. E. Avery, *ib.*, **19**. 270, 1860.

[5] G. Gore, *Journ. Chem. Soc.*, **15**. 104, 1863 ; C. E. Avery, *Chem. News*, **19**. 270, 1869.

[6] M. H. Klaproth, *Analytical Essays*, London, **1**. 50, 1801.

[7] M. W. Iles, *Eng. Min. Journ.*, **31**. 58, 1881 ; *Chem. News*, **43**. 78, 1881 ; C. A. Burghardt, *ib.*, **61**. 260, 1890 ; *Proc. Manchester Lit. Phil. Soc.*, (4), **3**. 171, 1890. See pages 266, etc.

[8] S. Kern, *Chem. News*, **35**. 203, 1877 ; D. Lindo, *ib.*, **60**. 14, 33, 41, 1889 ; L. H. Freidburg, *ib.*, **62**. 22, 32, 1890 ; *Journ. Amer. Chem. Soc.*, **12**. 134, 1890 ; W. Knopp, *Ber. König. Sachs. Ges. Wiss.*, 33, 1882 ; *Zeit. anal. Chem.*, 22, 558, 1883 ; *Chem. News*, 49, 62, 1884 ; E. Mallard, *Ann. Chim. Phys.* (4), **28**. 86, 1873. F. Stolba (*Sitzber. könig. Böhm. Ges. Wiss.*, 1885 ; *Zeit. anal. Chem.*, **25**. 378, 1886) recommends placing a layer of sodium chloride over the charge in the crucible before the mixture is heated.

[9] See page 163. C. F. Chandler, *Pogg. Ann.*, **102**. 446, 1857.

[10] C. Holthof, *Zeit. anal. Chem.*, **23**. 498, 1884 ; *Chem. News*, **51**. 18, 1885.

[11] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 630, 1852 ; J. J. Berzelius, *Pogg. Ann.*, **4**. 152, 1824 ; W. B. Giles, *Chem. News*, **99**. 25, 1909 ; M. H. Bedford, *Journ. Amer. Chem. Soc.*, **27**. 1216, 1905.

[12] J. L. Smith, *Amer. J. Science* (2), **40**. 248, 1865 ; *Chem. News*, **12**. 220, 1865 ; W. H. Worthington, *Min. Science*, **63**. 521, 1911.

IV. *Calcining the Silicate with an Alkaline Earth.*—Oxide, carbonate, etc.

(*a*) Calcium carbonate or oxide, alone or with calcium chloride.[1]

(*b*) Calcium carbonate with ammonium chloride.[2]

(*c*) Calcium sulphate.[3] This was used by von Hauer for lepidolite.

(*d*) Barium oxide or carbonate or nitrate.[4]

V. *Fusion with Lead or Bismuth Compounds.*

(*a*) Lead oxide.[5] This method is sometimes used in determining the total water in clay by Jannasch's process. The lead oxide retains fluorine, boron, etc.

(*b*) Lead carbonate.[6]

(*c*) Lead chromate.[7]

(*d*) Fusion with bismuth oxide or nitrate.[8]

VI. *Fusion with Boron Compounds.*

(*a*) Boric oxide, or boric acid.[9] This process promises to be useful for the determination of silica in the presence of fluorides, since, it is stated, the fluorine is evolved as boron fluoride—BF_3—not as silicon fluoride—SiF_4.

(*b*) Borax.[10] According to Wells, borax and boric anhydride attack platinum quite appreciably during high-temperature fusions.

(*c*) Potassium borofluoride mixed with potassium carbonate.[11] This mixture was used by Stolba for opening up zircons (4 of flux, 1 of powdered zircon).

VII. *Electrical Current.*—Several attempts have been made to decompose certain silicates and minerals while exposed to the joint effect of acids and an electric current, but with success only in special cases.[12]

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[1] F. Glinka, *Journ. Russ. Chem. Soc.*, **24.** 456, 1892; L. R. von Fellenberg-Rivier, *Zeit. anal. Chem.*, **5.** 179, 1866; H. Cormimbeuf, *Ann. Chim. Anal.* **15.** 295, 1910; H. St C. Deville, *Ann. Chim. Phys.* (5), **61.** 309, 1861; *Chem. News*, **4.** 255, 1861; E. Bonjean, *ib.*, **80.** 240, 1899; H. Rocholl, *ib.*, **41.** 234, 1880.

[2] J. L. Smith, *Amer. J. Science* (2), **50.** 269, 1871.

[3] F. Stolba, *Zeit. anal. Chem.*, **16.** 99, 1877.

[4] G. Werthier, *Journ. prakt. Chem.* (1), **91.** 321, 1864; H. Abich, *Pogg. Ann.*, **50.** 128, 341, 1840; P. Berthier, *ib.*, **14.** 100, 1828; J. W. Döbereiner, *ib.*, **14.** 100, 1828; L. R. Fellenberg-Rivier, *Zeit. anal. Chem.*, **9.** 459, 1870; W. Hempel, *ib.*, **52.** 86, 1913; G. Gore, *Journ. Chem. Soc.*, **15.** 104, 1862; J. J. Berzelius, *De l'Analyse des Corps Inorganiques*, Paris, 72, 1827; M. H. Klaproth, *Beiträge zur Kenntniss der Mineralkörper*, Berlin, **3.** 240, 1802.

[5] P. Berthier, *Ann. Chim. Phys.* (2), **17.** 28, 1821; G. Bong, *Zeit. anal. Chem.* **18.** 270, 1878; P. Jannasch and H. J. Locke, *Zeit. anorg. Chem.*, **6.** 168, 321, 1894 (for topaz); A. Leclerc, *Compt. Rend.*, **125.** 893, 1897; *Chem. News*, **77.** 27, 1898.

[6] P. Jannasch, *Ber.*, **26.** 1497, 2909, 1893; **27.** 2228, 1894; *Zeit. anorg. Chem.* **8.** 364, 1893; *Chem. News*, **71.** 51, 1895.

[7] P. Jannasch, *Ber.*, **22.** 221, 1889.

[8] W. Hempel and R. F. Koch, *Zeit. anal. Chem.*, **20.** 496, 1881; *Chem. News*, **45.** 81, 1882 (nitrate); T. M. Chatard, *Amer. J. Science* (3), **29.** 379, 1889; *Chem. News*, **50.** 279, 1884. (oxide).

[9] H. Davy, *Phil. Trans.*, **85.** 231, 1805; P. Jannasch, *Ber.*, **28.** 2822, 1896; P. Jannasch and O. Heidenreich, *Zeit. anorg. Chem.*, **12.** 208, 219, 1896; P. Jannasch and H. A. Weber, *Ber.*, **32.** 1670, 1899; H. A. Weber, *Ueber die Aufschliessung der Silikate durch Borsäureanhydrid*, Heidelberg, 1900; K. Pfeil, *Ueber die Aufschliessung der Silikate und anderer schwer zersetzbar Mineralien mit Borsäureanhydrid*, Heidelberg, 1901; E. Rupp and F. Lehman, *Chem. Ztg.*, **35.** 565, 1911.

[10] C. Rammelsberg, *Zeit. deut. geol. Ges.*, **24.** 69, 1872; W. Suida, *Tschermak's Mitt.* (1), **5.** 176, 1876; *Zeit. anal. Chem.* **17.** 212, 1878; J. S. C. Wells, *School Mines Quart.*, **12.** 295, 1891; *Chem. News*, **64.** 294, 1891.

[11] F. Stolba, *Chem. News*, **49.** 174, 1884.

[12] E. F. Smith, *Ber.*, **23.** 2276, 1890; **130.** 152, 1892; L. F. Frankel, *Chem. News*, **65.** 54, 66, 1892; M. Mayençon, *ib.*, **76.** 24, 1897.

§ 81. Sodium Carbonate for Silicate Fusions.

In most silicate analyses, the mineral is broken down by fusion with anhydrous sodium carbonate—a plan first used by T. Bergmann in the eighteenth century. Obviously, the sodium carbonate must be free from impurities which are going to be determined in the fused silicate.[1] For instance, if sulphur is going to be determined, the carbonate must be free from sulphur compounds. The total impurities — silica, alumina, etc. — should not exceed 0·01 per cent. If 10 grms. of such a carbonate be taken for the analysis, the maximum error for the impurities in the sodium carbonate will not then exceed 0·1 per cent. The impurities can be determined by a blank analysis.

Potassium carbonate fuses at about 885°, and sodium carbonate at 810°,[2] while a mixture of equimolecular proportions fuses at about 690°. The fusion curve for all possible mixtures is indicated in fig. 93. The so-called "fusion mixture" (sodium carbonate, 4 parts by weight; potassium carbonate, 5 parts) is the most fusible mixture of these two carbonates. Hence, this mixture is sometimes recommended for opening up silicates in preference to sodium carbonate alone, because of its greater fusibility. This point is, however, of little importance, because the temperature of silicate fusions is generally greater than the melting point of either salt alone; and there is no difficulty in maintaining the necessary temperature.

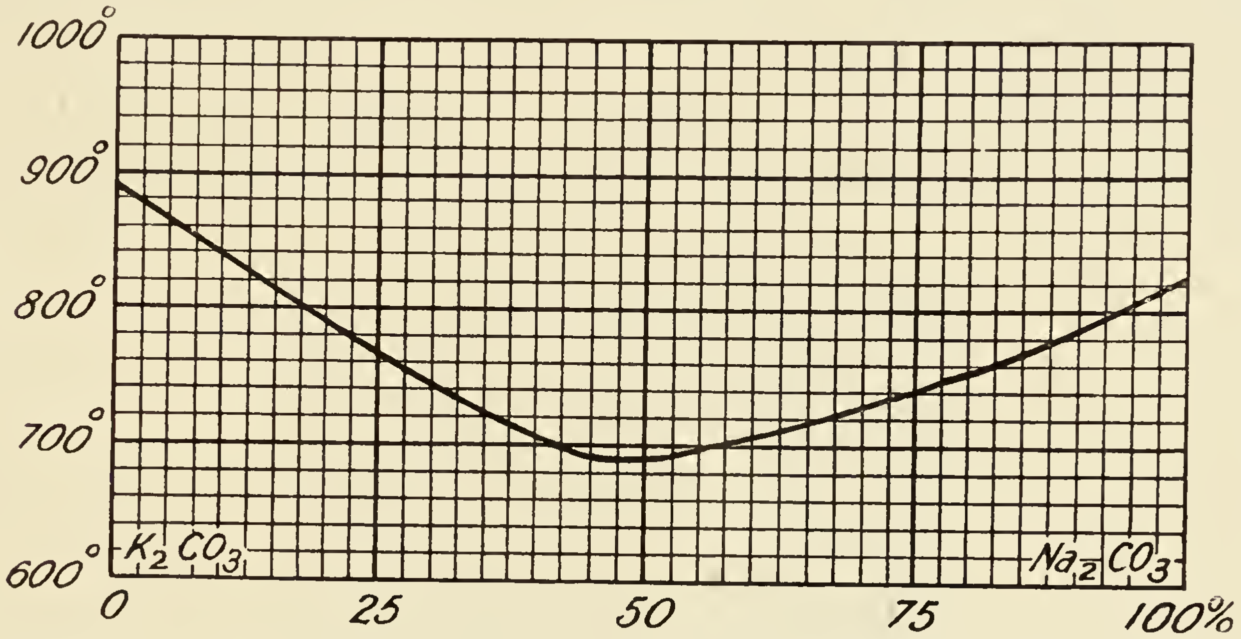

FIG. 93.—Melting points of mixtures of sodium and potassium carbonates.

Dittrich[3] has pointed out that potassium salts are washed from the different precipitates, later on, with greater difficulty than sodium salts. In illustration, Reidenbach shows that a "magnesia" precipitate made in a 3N-solution of potassium chloride retains nearly twice the weight of occluded salt as a precipitate made under similar conditions in a 3N-solution of sodium chloride. Still further, Smith has shown that the resulting cake with potassium carbonate dissolves in water with greater difficulty than when sodium carbonate is used.

Platinum crucibles are slightly attacked by the fusion with sodium carbonate. Koninck[4] says that 6 grms. of fusion mixture when melted in a platinum crucible over a Bunsen's burner, and then over a blast, caused the platinum crucible to lose in weight 0·0010 grm. Hence, Koninck says that in exact analyses the platinum should be removed by treatment with hydrogen sulphide in acid solution. Koninck's numbers are higher than those obtained in my own experience with sodium carbonate fusions. There is also no need to remove the platinum until after the potassium pyrosulphate fusion, as indicated on page 186.

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[1] J. L. Smith (*Chem. News*, **30**. 234, 1874) on the preparation of pure potassium and sodium carbonates for silicate fusions. Excellent sodium carbonate can now be purchased with a guaranteed composition.

[2] H. le Chatelier, *Bull. Soc. Chim.* (2), **47**. 300, 1887.

[3] M. Dittrich, *Anleitung zur Gesteinanalyse*, Leipzig, 5, 1905 ; R. Reidenbach, *Ueber die quantitative Bestimmung des Magnesiums als Magnesiumpyrophosphat*, Kusel, 69, 1910.

[4] L. L. de Koninck, *Zeit. anal. Chem.*, **18**. 569, 1879.

§ 82. Opening Clays and Silicates by Fusion with Sodium Carbonate.

Charging the Crucible.—Either 1 grm. of the powdered clay dried at 110°, or the clay remaining in the crucible after the loss on ignition[1] has been determined, is mixed with six to eight times its weight of anhydrous sodium carbonate, by adding the carbonate to the crucible and thoroughly mixing the contents of the crucible by means of a spatula. Take care to get plenty of sodium carbonate at the bottom of the crucible. Two more grams of sodium carbonate are introduced and levelled down with the spatula. The spatula is also cleaned by the sodium carbonate at the same operation.

The Fusion.—The crucible is placed slightly inclined on a platinum or pipe-clay triangle, so that the flame does not completely envelop the crucible (fig. 94).

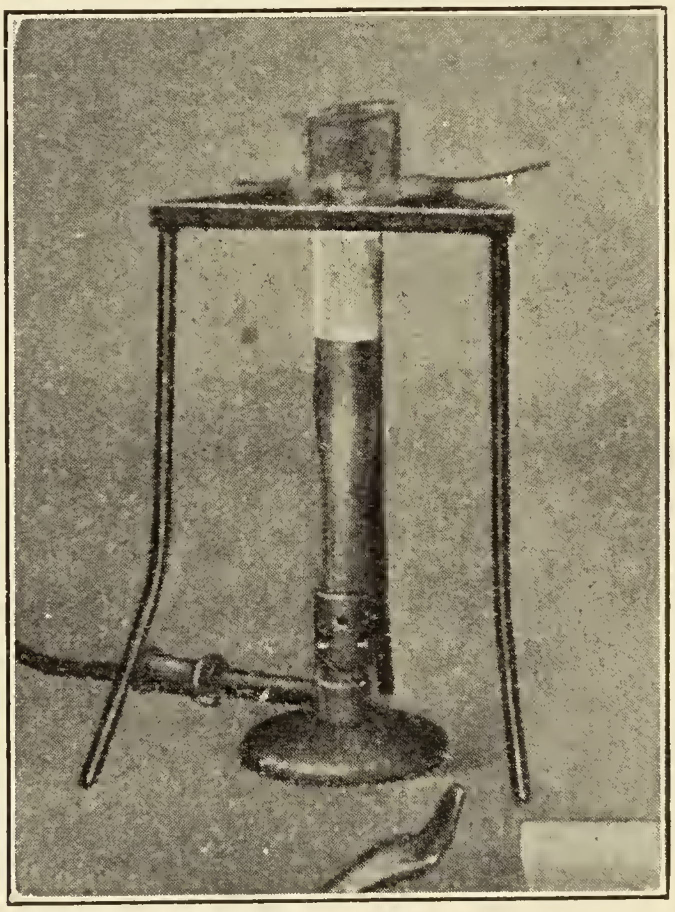

Fig. 94.—Fusion of silicate with sodium carbonate.

The object is to keep the atmosphere inside the crucible as oxidising as possible. The lid is placed on the crucible, and the latter is heated over a low flame with the bottom of the crucible at a dull red for a quarter of its length. This drives off the carbon dioxide without spluttering. In about 15 minutes the crucible is heated to bright redness by means of, say, a Teclu's or a Méker's burner for about 15 minutes. The contents of the crucible will then probably be in a state of quiet fusion,[1] and gas bubbles will have ceased to come off. Little if any spluttering of the contents of the crucible on to the inside of the lid will have taken place if the operation has been properly performed.

---

[1] If the clay sinters into clots when the loss on ignition is determined, it is best to work with an uncalcined sample, because sintered masses are decomposed with difficulty by the fused carbonate.

Cooling the Crucible.—The crucible is then removed from the flame by the platinum-pointed tongs (fig. 63 is the better type), and, while still red-hot, placed under the water tap so that a gentle stream of water flows from the tap on the sides of the crucible;[2] or else dip the crucible in a dish of cold water. Not a drop of water must be permitted to splash inside the crucible. By giving the contents of the crucible a rotary motion as the contents begin to solidify, it is possible to spread the contents over the sides and the bottom and render the subsequent removal of the cake easier. Let the crucible cool on a slab of granite, marble, or an unglazed tile. A green-coloured cake indicates the presence of manganese—sodium manganate—but manganese may be present without showing the green colour if the inside of the crucible, during the fusion, was not sufficiently oxidising. The dirty brown colour of highly ferruginous clays might also obscure the manganese green.

Transfer of the Cake to the Basin.—When cold, the crucible is half filled with water, and a gentle heat applied without allowing the contents to boil. If the crucible be not dented, and has been allowed to cool a sufficient length of time, the cake will quickly loosen,[3] and may be tipped into a 250-c.c. evaporating basin (better a platinum basin).[4] The cake is dissolved in 100–200 c.c. of water,[5] and about 20 c.c. of concentrated hydrochloric acid are poured down the inside of the evaporating basin, a few drops at a time, so as not to lose any of the liquid by effervescence; or better, cover the basin with a clock-glass, lift up the cover a little, and add the acid from a pipette. Any portion of the cake adhering inside the crucible must be removed by means of a "policeman" and hydrochloric acid.[1] Any white spots which appear on the crucible after it is supposed to have been cleaned must be transferred to the basin. The crucible lid is also cleaned and the washings transferred to the basin.

---

[1] Highly siliceous clays, flint, and felspar usually give clear transparent fusions; while Cornish stone, clays, and pottery bodies, even though completely decomposed, form more or less turbid liquids. Highly aluminous clays form viscid liquids; siliceous clays, limpid liquids. It is a good plan to use rather more sodium carbonate for the former type of silicates.

[2] Some object to sudden cooling by a blast of air; dipping in cold water, etc. The sudden cooling is said to shorten the life of the crucible (C. Stöckmann, *Zeit. anal. Chem.*, 15. 283, 1876). I have not noticed any deterioration in a crucible which has been used for over 200 fusions, and cooled as described in the text. It promises to do an indefinite number more. A similar remark might be applied to several other crucibles I have used.

[3] Do not "squeeze the platinum crucible between the finger and thumb to loosen the fused mass," as one writer recommends.

[4] To mark porcelain vessels, scratch a mark on the vessel with a diamond. Smear platinum chloride over the mark, and when it is almost dry, wipe (not wash it off). When fired in a muffle, the vessel is marked with metallic platinum (B. Blount, *Chem. News*, 56. 66, 1887; A. A. Kelly, *ib.*, 83. 95, 1901). H. Jervis (*Chem. News*, 83. 118, 1901) recommends marking the crucibles with ink, and W. C. Kriescher (*Chem. News*, 83. 130, 1901) with blue pencils and then firing. C. Reinhardt (*Zeit. anal. Chem.*, 23. 42, 1884) recommends marking in coloured enamel, finely powdered, and ground in aniseed or lavender oil. This is marked on the porcelain, and fired in a muffle. P. A. Yoder, *Chem. Eng.*, 15. 102, 1911; *Journ. Ind. Eng. Chem.*, 4. 567, 1912; C. D. Mason, *ib.*, 4. 691, 1912.

[5] Analysts are frequently puzzled why the silica from a given silicate fusion is sometimes gelatinous and difficult to filter and wash, and at other times it appears more or less pulverulent and easy to wash. In many cases this is due to the way the fused cake in the crucible is treated. The pulverulent form is obtained by dissolving the cake in a large volume of water, say 200 c.c., and then acidifying the solution. This large volume may take longer to evaporate than when the acid is added to a concentrated solution; but if the concentrated solution be acidified, the silica is more likely to separate in the gelatinous form. In the latter case, a considerable amount of time will be spent in filtering and washing, and the result will be less satisfactory. The silica which separates from the dilute solutions also appears to be of greater purity. When the silica separates from concentrated solutions, it probably encloses particles of liquid not easily removed by washing. These results are not so marked when considerable amounts of alumina are present, but in any case the different effects are noticeable.—D. Lindo, *Chem. News*, 60. 14, 33, 41, 1889. Some consider that the addition of alcohol to the solution makes the silica separate during evaporation in the granular form, which is easily filtered and washed. It is also claimed that two evaporations are not then necessary.

The basin will now be half or three-quarters full of liquid. It is placed on the water bath and the disintegration of the cake is assisted from time to time by means of the spatula. The cake will not dissolve very readily if the fusion has been conducted at a very high temperature. Flakes of silicic acid may now be observed floating about the liquid. If any gritty particles remain in the basin, the decomposition by the sodium carbonate was not complete.[2] In that case it is best to start again.[3]

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[1] The less dented and the smoother the crucible, the more easily is the cake removed. A very obstinate cake is dissolved in the crucible on the water bath, with or without the addition of hydrochloric acid, and the contents emptied from time to time into the evaporating basin. Fresh water or acid is introduced into the crucible. If the acid be used with a green cake, chlorine may be evolved and attack the crucible. In that case, a few drops of alcohol will destroy the manganate, and prevent the generation of chlorine. F. Stolba (*Zeit. anal. Chem.*, 25. 378, 1886) pours the melted mass on a suitable slab ; J. Herman (*West. Chem. Met.*, 5. 476, 1909) pours the melted mass into a beaker containing 50 c.c. of water. In that case, the mass should be a limpid fluid when poured, or an explosion might result. Bisulphate and caustic alkali fusions must not be poured into water. L. L. de Koninck (*Zeit. angew. Chem.*, 1. 569, 1888) recommends inserting a piece of platinum wire, bent at one end in the form of a spiral, into the fused mass when fusion is complete ; when cold, the other end of the platinum wire is suspended from a glass rod, or a retort clamp on a retort stand, so that the crucible hangs a few millimetres above the triangle. On heating the crucible quickly, the crucible falls into the triangle and the "melt" remains suspended on the platinum wire separated from the crucible. Both it and the residue in the crucible can then be dissolved in the regular manner.—E. R. E. Müller, *Chem. Ztg.*, 32. 880, 1908.

[2] Magnetite and ilmenite may escape decomposition by the fusing carbonate, and yet be subsequently dissolved by the hot hydrochloric acid. According to P. W. Shimer (*Journ. Amer. Chem. Soc.*, 16. 501, 1894) in the analysis of blast-furnace slag, spinel—magnesium silicate or aluminate—is not decomposed by fusion with alkali carbonates. By treating the slag with hydrochloric and hydrofluoric acids, and afterwards fusing the residue with sodium carbonate, the spinel can be isolated as a crystalline powder. Treatment with concentrated sulphuric and hydrofluoric acids decomposes the spinel. This substance, therefore, if present, will be broken down at a later stage of the analysis—correction for silica.

[3] If the amount of sample available be small, the undecomposed material can be collected in a filter paper, ignited, and re-fused with sodium carbonate.

CHAPTER XII.

THE DETERMINATION OF THE SILICA.

§ 83. The Determination of Silica.

First Evaporation.—The hydrochloric acid solution of the cake contains the various constituents of the clay in solution principally as chlorides. These are subsequently removed one by one. First the silica. Evaporate the contents of the basin to dryness on the water bath, protected from dust.[1] There is no appreciable loss of the constituents to be determined in the solution during the evaporation.[2] Heat the dry residue in an oven (fig. 90), between 109° and 110°, or leave it on the water bath, until the smell of the hydrochloric acid has disappeared.[3] Pour about 5 c.c. of concentrated hydrochloric acid and 30–40 c.c. of water on the residue; warm on a water bath 10 to 15 minutes; break up any coarse lumps with the spatula or "policeman"; decant the clear into, say, a 9-cm. filter paper, and collect the filtrate in a 400-c.c. beaker. Add more water and acid to the basin, warm again; again decant on to the filter paper, repeat the treatment, and finally transfer the contents of the dish to the filter paper.[4] Wash with cold water until all the chlorides have been washed out. Test a drop of the filtrate with a drop of silver nitrate solution; if there be no turbidity, the washing is complete.

Second Evaporation.—The filtrate is transferred to the same basin as was employed in the first evaporation, and the solution evaporated to dryness as before. Digest in dilute hydrochloric acid; filter through a 7-cm. filter paper, and collect the filtrate in a 400-c.c. beaker. Take special care to remove all particles of silica which may adhere to the basin by rubbing with a "policeman," etc.[1] Wash with cold water as before. The filtrate will occupy 150 to 200 c.c.[2]

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[1] A. V. Meyer's evaporating funnel, fig. 95, is suitable (*Ber.*, **16**. 3000, 1883). The evaporating funnel has been raised a little in the diagram.

[2] F. Kehrmann and B. Flürscheim (*Zeit. anorg. Chem.*, **39**. 105, 1904) refer to a loss of silica by evaporation with acids; but C. Freidheim and A. Pinagel (*ib.*, **45**. 410, 1905) show that the loss probably occurred during the (careless) filtration, not during the evaporation. K. F. Föhr (*Berg. Hütt. Ztg.*, **41**. 252, 1882; *Chem. News*, **46**. 40, 1882; W. Skey, *ib.*, **16**. 207, 1867; D. H. Browne, *Journ. Anal. App. Chem.*, **5**. 342, 1891; A. Vogel, *Neues Rept. Pharm.*, **18**. 157, 1869) has stated that some ferric chloride is lost during the evaporation of the acidified solution, but R. Fresenius (*Zeit. anal. Chem.*, **6**. 92, 1867) and L. L. de Koninck (*Zeit. angew. Chem* , **11**. 258, 1899; H. P. Talbot, *Amer. Chem. Journ.*, **19**. 52, 1897; R. W. Atkinson, *Chem. News*, **49**. 217, 1884; H. Seward, *ib.*, **16**. 219, 233, 1867) have shown that the statement is erroneous. There is no appreciable loss either during the evaporation or during the drying of the residue at 130°. If, however, residues containing ammonium chloride or aqua regia be so treated, there is, according to Talbot, an appreciable loss of iron.

[3] For the influence of the drying temperature on the final result, see page 173 *et seq.*

[4] Washing with hot water is inclined to precipitate basic chlorides of iron with the silica. Basic iron salts, for instance, are precipitated on boiling slightly acid solutions in the presence of much alkali salts (U. S. Pickering, *Journ. Chem. Soc.*, **37**. 807, 1880). In that case, the ignited silica is not white, but dirty brown. Cold water is therefore best for washing the silica of ferruginous clays, and this the more as sodium chloride is not much more soluble in hot water (39·8 grms. per 100 c.c. at 100°) than in cold water (35·8 grms. in 100 c.c. of water at 10°). But, other things being equal, hot solutions filter more rapidly than cold solutions. W. F. Hildebrand (*Bull. U.S. Geol. Sur.*, **422**. 92, 1910) does not recommend washing with dilute hydrochloric acid as advocated by C. Freidheim and A. Pringel (*Zeit. anorg. Chem.*, **45**. 411, 1905).

Ignition of the Silica.—The free edges of the filter paper are folded down on the silica, and both filter papers, while still moist, are placed in a weighed platinum crucible. The paper containing the bulk of the silica is placed in the crucible first. The triple folds of the filter paper are placed uppermost to facilitate oxidation. Heat the crucible and contents slowly some distance away

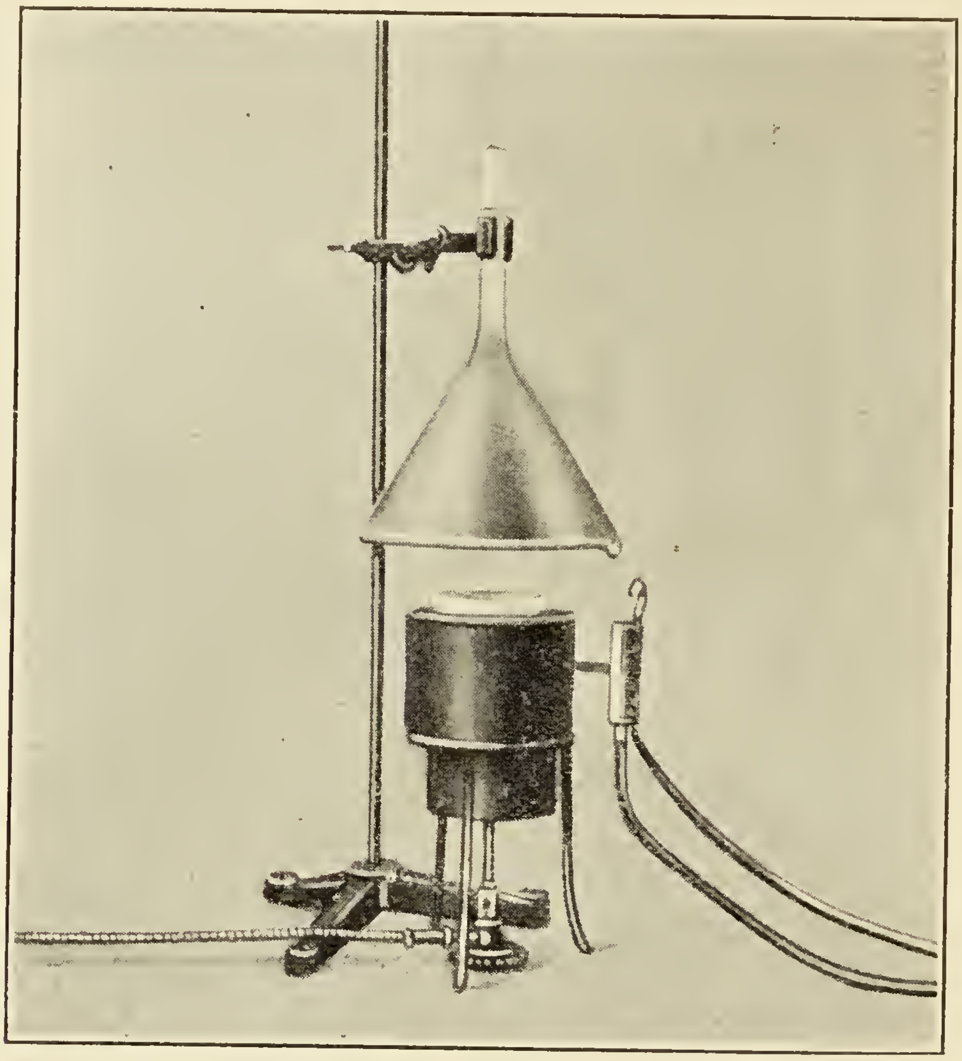

FIG. 95.—Evaporation for silica.

from the small flame of the Bunsen's burner until the paper is thoroughly charred. An Argand burner and chimney (fig. 112) is useful for this purpose. Then gradually raise the temperature, but not high enough to ignite the vapours issuing from the mouth of the crucible, or there will be a danger of loss owing to the draught set up by the escaping gases whirling the light powdered silica out of the crucible. When the paper has all burned off, put the cover on the crucible, and blast the silica for 20 to 30 minutes in order to dehydrate the silica and render it less hygroscopic. Cool in a desiccator and weigh.[3] The silica should of course be ignited until no further loss in weight occurs, but experience shows that the above period is ample with a good blast.[1] Record the weight as indicated below : " Uncorrected silica plus crucible."

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[1] Dry the porcelain basin, when any traces of silica not transferred to the filter paper can be easily detected as white spots. F. L. Kortright, *Chem. Eng.*, 5. 19, 1905; O. Knöfler (*Zeit. anal. Chem.*, 28. 673, 1889) recommends a dark underglaze colour in the interior of evaporating basins to show up any traces of residues or precipitates like aluminium hydroxide, etc. F. Moldenhauer (*Zeit. anal. Chem.*, 50. 754, 1911) recommends platinum basins.

[2] A trace of silica passes into the second filtrate, and is partly recovered at a later stage of the analysis, as "extra silica."

[3] The lower the temperature at which the silica is calcined, the more hygroscopic the resulting powder. A. Souchay (*Zeit. anal. Chem.*, 8. 423, 1869) states that precipitated silica calcined at a low temperature absorbed 14·38 grms. of hygroscopic moisture per 100 grms. of

Impurities in the Silica.—The silica so obtained is not quite pure. It probably contains small quantities of titanic oxide, phosphoric oxide, alumina, and ferric oxide.[2] Add 5 c.c. of water [3] and about 5 drops of concentrated sulphuric acid. The latter is necessary to prevent the volatilisation of the titanium fluoride [4]—TiF_4 (and possibly also some aluminium fluoride—AlF_3). Add hydrofluoric acid [5] carefully, a few drops at a time, to prevent loss by the violent effervescence which sometimes occurs. The crucible is filled not quite half full with hydrofluoric acid. Warm the crucible on a hot plate over a small flame in the fume chamber until the contents are almost dry. Add 2 or 3 c.c. more hydrofluoric acid, and take the contents of the crucible to dryness on the hot plate. The radiator (page 112), or the burner illustrated in fig. 96, is useful in taking sulphuric acid to dryness without loss by spurting. The crucible is heated from above downwards, and the flame can be so adjusted that evaporation proceeds quietly. Heat the crucible to bright redness, and blast the

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silica ; silica calcined at the full temperature of a Bunsen's burner, 2·00 grms. per 100 grms. of silica ; and silica calcined in a blast absorbed 0·09 grm. of hygroscopic moisture per 100 grms. of silica. Powdered quartz under similar conditions absorbed no hygroscopic moisture—J. W. Mellor and A. D. Holdcroft, *Trans. Eng. Cer. Soc.*, 9. 94, 1911.

[1] This point should, however, be verified. See also T. Bauer (*Tonind. Ztg.*, 37. 89, 1913) for the difficulty in getting rid of the last traces of hydrochloric acid.

[2] And, in special cases, lead sulphate, calcium and barium sulphates, tin oxide, antimony oxide, tungsten oxide, and basic salts. Silica is very liable to retain phosphoric and tungstic acids—W. Skey, *Chem. News*, 16. 187, 1867 ; and also arsenic and tin oxides—if present.

[3] Be careful in adding liquids to dry powders (especially if hot). There is a tendency for some of the powder to be dissipated as a "cloud of dust"—E. Jordis and W. Ludewig, *Zeit. anorg. Chem.*, 47. 180, 1905.

[4] E. Riley, *Journ. Chem. Soc.*, 12. 13, 1860 ; P. Holland, *Chem. News*, 59. 27, 1889 ; P. Truchot, *Rev. Gén. Chim.*, 18. 173, 1905. Thus, Holland has shown that titanic oxide is lost by fuming with hydrofluoric acid when sulphuric acid is absent, but not when it is present:

Sulphuric acid.	TiO_2 present.	TiO_2 found.
None present . .	0·0466	0·0340
Present . . .	0·0414	0·0413
Present . . .	0·0520	0·0520

E. Wedekind (*Ber.*, 44. 1753, 1911) has also shown that the presence of sulphuric acid considerably reduces the loss of zirconium when fuming with hydrofluoric acid to drive off the silica.

[5] Hydrofluoric Acid.—The acid must be free from non-volatile impurities—K. F. Stahl, *Zeit. öffent. Chem.*, 3. 13, 1896 ; A. H. Allen, *Analyst*, 21. 87, 1896 ; B. Blount, *ib.*, 21. 87, 1896. Hydrofluosilicic acid, derived from the silica in the fluorspar used in the manufacture of the hydrofluoric acid, is a common impurity. Sulphuric acid, as well as hydrofluosilicic acid, may distil over with the hydrofluoric acid. The acid may also contain substances which reduce potassium permanganate (pages 195, 226, and 463). For apparatus for working with hydrofluoric acid, see G. Foord, *Chem. News*, 30. 191, 1874 (apparatus for pouring) ; E. Cohen, *Natur. Ver. Neuvorpommern Rugen*, 20. 1, 1889 ; H. C. Andersch, *Chem. Ztg.*, 12. 1475, 1888 ; R. Benedict, *ib.*, 15. 881, 1891 ; E. Hart, *Journ. Anal. App. Chem.* 3., 372, 1889 (bottles for) ; G. P. Vanier, *ib.*, 4. 48, 1890 (pipette). Preparation of pure acid : R. Hamilton, *Chem. News*, 60. 252, 1889 ; W. Hempel, *Ber.*, 18. 1434, 1885 ; A. P. Stuart, *Amer. Chem.*, 2. 384, 1871. A drop of hydrofluoric acid on the skin produces a serious "burn." According to M. Kessler (*Chem. News*, 8. 17, 1863), the "first aid" treatment for hydrofluoric acid on the hands, etc., is to use lint wetted with ammonium acetate and inject the same solution into the blisters. If the acid has touched parts of the skin difficult to moisten, *e.g.*, under the nails, concentrated ammonia will give the best results. The excruciating pain which attends the first application of the ammonia is transient.

residue five minutes.[1] Weigh the crucible and contents,[2] and enter the result as "crucible plus residue." The difference between this weight and the preceding represents the silica.[3] A minute quantity of silica has yet to be added to the silica so determined—the "extra silica" of page 185.

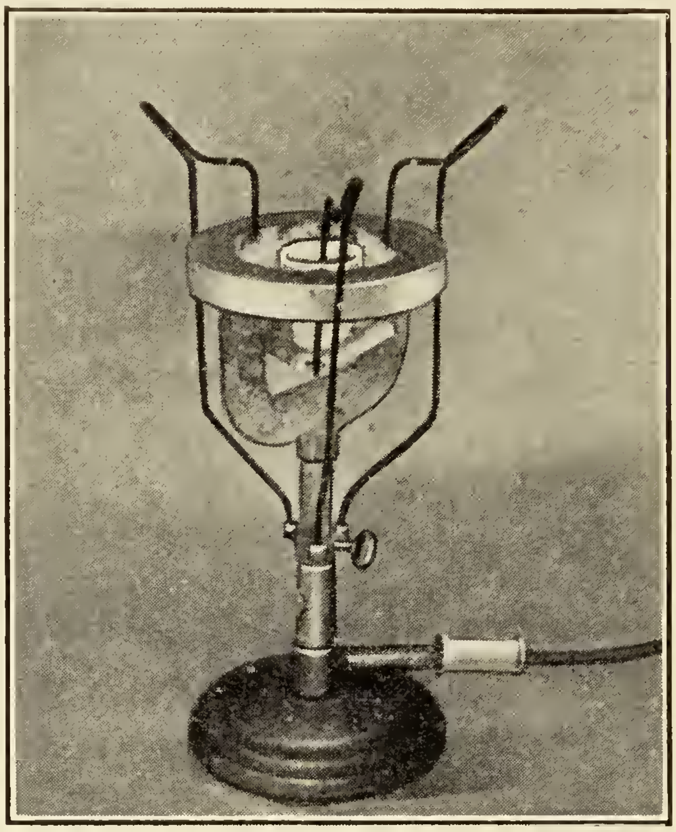

FIG. 96.—Ring burner.

It is here assumed that the residue in the crucible is free from lime, magnesia, and alkaline salts, and that the crucible only contains constituents belonging to the ammonia precipitate. Bloor[4] has investigated the validity of this assumption by analysing the residues. He found among other determinations that :—

Table XXVII.—Composition of the Silica Residues.

Total residue.	Alumina.	Ferric oxide.	Magnesia.	Lime.
0·0072	0·0023	0·0008	0·0022	0·0007
0·0062	0·0006	0·0020	0·0014	0·0005
0·0080	0·0018	0·0020	0·0007	0·0020
0·0036	0·0000	0·0010	0·0014	0·0004
0·0074	0·0028	0·0018	0·0000	0·0020
0·0046	0·0006	0·0018	0·0000	0·0023
0·0080	0·0025	0·0031	0·0012	0·0008
0·0013	0·0000	0·0000	0·0005	0·0012

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[1] It is important to drive off all the hydrofluoric acid, or troubles with the alumina will follow later.

[2] If a sand bath is used, see that the outside of the crucible is free from sand grains before the crucible is weighed. The burner shown in fig. 96 can frequently be used instead of the hot plate or sand bath. The Bunsen's flame, if adjusted very low, is also satisfactory—W. Gibbs, *Chem. News*, **28**. 30, 1873.

[3] S. V. Peppel reports that with low-grade limestones he has found that the loss in weight obtained on treating the insoluble residue with hydrofluoric and sulphuric acids is sometimes greater than the amount of silica actually present—H. E. Ashley, *Chem. News*, **90**. 274, 1904.

[4] W. R. Bloor, *Journ. Amer. Chem. Soc.*, **29**. 1603, 1907 ; C. Meineke, *Rep. anal. Chem.*, **7**. 214, 1887 ; E. Jordis, *Zeit. anorg. Chem.*, **45**. 362, 1905.

Hence, Bloor concludes that the residue "is contaminated to some degree by the main constituents of the clay. The amount of contamination by substances other than ferric oxide and alumina is, however, except in extreme cases,[1] so small that it may be neglected unless extreme accuracy is required"; in that case the residue can be taken up with a little sodium carbonate, and the acid solution of the fused mass added to the main solution.

Weighings.—The results of the silica weighings in the above operations, together with the "extra silica" from a later operation, will be entered in the notebook somewhat as follows:—

Silica and crucible	21·0603 grms.
Crucible empty[2]	20·4530 ,,
Uncorrected silica	0·6073 grm.
Residue and crucible	20·4552 grms.
Crucible empty	20·4530 ,,
Residue	0·0022 grm.
Extra silica and crucible	22·9531 grms.
Crucible, etc., after action of HF	22·9522 ,,
Extra silica	0·0009 grm.
Silica uncorrected	0·6073 grm.
Residue	0·0022 ,,
Silica	0·6051 ,,
Extra silica	0·0009 ,,
Silica found	0·6060 ,,
Correction for silica in reagents	0·0008 ,,
Total silica	0·6052 ,,

Errors.—The following results were obtained in eight independent determinations with one sample of clay:—0·6052; 0·6048; 0·6047; 0·6046; 0·6053; 0·6044; 0·6044; 0·6043 grm. The mean is 0·6047 grm., or 60·47 per cent., with a deviation of about ± 0·07. The deviations will be different with clays containing different amounts of silica. But if this particular sample be analysed by another analyst, we should expect the silica to come somewhere between 60·40 and 60·54 per cent. The variations obtained with a number of analyses as indicated above give an idea of the errors liable to affect particular determinations, but they tell nothing about the presence or absence of constant errors—say, errors due to the solubility of silica in the mother liquid, etc. The case of lithium, page 537, might be cited as an instructive example. These constant errors can rarely be checked, although an approximate idea can sometimes be obtained by control analyses with artificial mixtures containing known amounts of the constituents under investigation—page 247.[3]

Every method of analysis has its own peculiar sources of error. The principal sources of error in silica determinations are: (1) Imperfect decomposition of the silicate; (2) Loss by spurting when the acid is added to the carbonate fusion; (3) Imperfect transfer of the silica from dish to filter paper; (4) Tendency of silica to remain in a soluble condition after the baking at 109°; (5) Mechanical loss of fine particles of silica transported with the gases from the burning filter paper, and during the dehydration of the silica; (6) Contamination by the reagents, and by the porcelain vessel during evaporation; (7) And the loss of weight of the crucible itself during the prolonged blasting.

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[1] *E.g.*, when the amount of magnesium or calcium in the original sample is high, as was the case with the third sample in the above table.

[2] The loss in weight by the blasting of the crucible was negligibly small for the small crucible employed. If the crucible lost appreciably in weight during the blasting, write: "Empty crucible plus loss in weight during blasting." See page 114.

[3] M. Stoermer (*Tonind. Ztg.*, 35. 453, 1911) considers that alumina is volatilised when the silica is heated with sulphuric and hydrofluoric acid. No appreciable loss can be detected under the conditions of the experiment described in the text.

Determination of Silica in the Presence of Fluorides.—If fluorine be present, as, say, calcium fluoride, part of the silica will be lost by volatilisation as silicon tetrafluoride—SiF_4—when the solution is evaporated to dryness. Supposing, in the extreme case, that all the fluorine be so evolved, the maximum possible error will be nearly equal to three-eighths of the calcium fluoride. The error becomes appreciable in the case of Cornish stone, which contains from 2 to 5 per cent. of calcium fluoride. In this case the silica and fluorine are to be separately determined, as indicated on page 640.

Determination of Silica in the Presence of Boric Oxide.—When borates are present, it is necessary to get rid of the boric oxide by adding methyl alcohol, saturated with hydrogen chloride, during the evaporation for silica, as indicated on page 589.

§ 84. The Theory of Silica Determinations.

When an aqueous solution of sodium silicate is treated with hydrochloric acid,[1] part of the silicate will be decomposed, forming sodium chloride and silicic acid, say, $H_{2n}SiO_{n+2}$. Conversely, when a solution of silicic acid is treated with sodium chloride, hydrochloric acid and sodium silicate are produced. These reactions are symbolised:

$$2n\mathrm{NaCl} + \mathrm{H}_{2n}\mathrm{SiO}_{n+2} \rightleftharpoons 2n\mathrm{HCl} + \mathrm{Na}_2\ \mathrm{SiO}_{n+2}.$$

The reversed arrows are intended to represent the fact that the reaction proceeds in each direction. When the speeds of the two reactions are the same, the system is in equilibrium, and the solution contains all four substances in certain definite proportions. If not, the system is not in equilibrium, and it will be doing its best to attain that condition. Whatever be the condition of the system after it has been evaporated to dryness, when the residue is taken up with dilute acid, a definite proportion of the silica in solution will be present as colloidal silicic acid,[2] and the rest as sodium silicate.

If all the soluble silicic acid in the dried residue could be converted into insoluble silicic acid by baking at a high temperature, the sodium silicate, when taken up with more hydrochloric acid, would be hydrolysed and furnish the same relative proportions of soluble silicic acid and sodium silicate as before. If the silicic acid so formed could be rendered insoluble by another evaporation, it follows that repeated evaporation to dryness and soaking the dried residue would transform practically all the silica into the insoluble condition, and the filtrate would be practically free from silica. Some analysts are under the impression that the action does occur, and recommend this procedure.[1]

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[1] Gelatinous orthosilicic acid—H_4SiO_4—is precipitated. This, when heated, or digested with sulphuric acid, forms metasilicic acid—H_2SiO_3 (R. Meldrum, *Chem. News*, **78**. 235, 1898); and this at 100°–110° forms the trisilicic acid—$H_2Si_3O_7$—which is insoluble in water and acids: at a high temperature the latter is converted into anhydrous silica.

[2] For the solubility of silica, see R. Bunsen, *Pogg. Ann.*, **61**. 265, 1847; E. Ludwig, *Zeit. anal. Chem.*, **9**. 321, 1870; C. Meineke, *Rep. anal. Chem.*, **7**. 214, 757, 1887; P. Jannasch and O. Heidenreich, *Zeit. anorg. Chem.*, **12**. 214, 1896; C. Winkler, *Chem. Centr.*, **4**. 673, 1859; J. W. Mellor and A. D. Holdcroft, *Trans. Eng. Cer. Soc.*, **10**. 1, 1911. For the alleged relatively greater solubility of silica in hydrochloric acid than in aqua regia, see G. C. Wittstein, *Zeit. anal. Chem.*, **7**. 433, 1868. For the solubility of silica in aq. ammonia, see page 183.

The percentage amount of water lost per hour in the earlier stages of the drying (110°) is very much greater than in the later stages. Indeed, the last stage of the dehydration requires an indefinitely long time for its completion.[2] This is illustrated by the gradual approach of the curve (silicic acid containing 23·9 per cent. water), fig. 97, to a horizontal line. If the temperature be raised, the transformation takes place much more rapidly and completely; but experience shows that the higher the desiccation temperature, the greater the amount of foreign matter associated with the silica. "This," says Gilbert,[3] "is probably due to the alumina being rendered insoluble in acids." For example :—

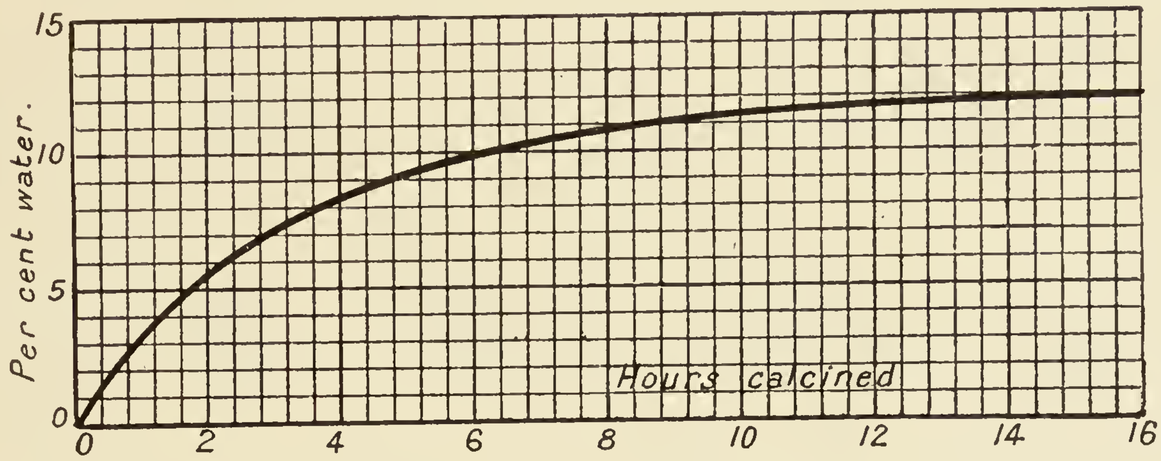

FIG. 97.—Effect of time occupied by drying at 110° on the dehydration of silicic acid.

Table XXVIII.—Effect of the Dehydration Temperature on the Determination of Silica in Aluminous Clays.

Total SiO_2 per cent.	Temperature.	Residue after first evaporation (per cent.).	Residue after second evaporation (per cent.).	SiO_2 in filtrate (per cent.).
64·15	100°	64·46	0·0018	0·0017
64·28	120°	64·19	0·0023	0·0032
64·55	280°	64·90	0·0070	0·0035

If the amount of alumina be high, the residue left after the removal of silica is greater the higher the drying temperature. In the case of calcareous slags (46 per cent. CaO), the calcium chloride in the residue seems to facilitate the dehydration of the silica and reduce the amount of silica soluble in the filtrate.

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[1] *E.g.*, G. Lunge, *Technical Methods of Chemical Analysis*, London, **1**. 581, 1908. M. Stoermer (*Tonind. Ztg.*, **35**. 453, 1911) considers that all the silica is converted into an insoluble form by evaporating the hydrochloric acid solution; baking at 130°; and soaking two hours with hydrochloric acid. He considers a second evaporation to be unnecessary, for it makes no difference whether or not the silica be filtered off before the second evaporation. The experimental results quoted in this chapter show that two evaporations with an intervening filtration are necessary for exact work; but see the section on abbreviated systems of analysis, page 242.

[2] J. M. van Bemmelen, *Zeit. anorg. Chem.*, **13**. 233, 1897; *Die Adsorption*, Dresden, 196, 1910. According to P. H. Walker and J. B. Wilson (*Circ. U.S. Dept. Agric.*, **101**. 1, 1912), a two-hours' ignition at the highest temperature obtainable with a Bunsen's burner suffices for the dehydration of silica, and three hours for alumina; there is then no risk of error owing to a change in weight of the platinum crucible.

[3] J. P. Gilbert, *Tech. Quart.*, **3**. 61, 1890; *Chem. News*, **61**. 270, 281, 1890; G. Craig, *ib.*, **60**. 227, 1889.

Table XXIX.—Effect of the Dehydration Temperature on the Determination of Silica in Calcareous Clays.

Total SiO_2.	Temperature.	Residue after first evaporation (per cent.).	Residue after second evaporation (per cent.).	SiO_2 in filtrate (per cent.).
41·28	100°	41·33	0·0013	0·0008
41·20	120°	41·32	0·0018	0·0006
41·52	280°	41·78	0·0029	0·0003

On the other hand, magnesium chloride seems to retard the dehydration at 100°; and at 280° it increases the amount of soluble silica in the filtrate. Thus, with a slag containing 35 per cent. of CaO and 15 per cent. of MgO :—

Table XXX.—Effect of the Dehydration Temperature on the Determination of Silica in Magnesian Clays.

Total SiO_2.	Temperature.	Residue after first evaporation (per cent.).	Residue after second evaporation (per cent.).	SiO_2 in filtrate (per cent.).
33·70	100°	33·67	0·0020	0·0023
33·80	120°	33·63	0·0028	0·0008
33·94	280°	33·81	0·0065	0·0052

Hillebrand[1] considers that magnesia begins to recombine with silica to form a magnesium silicate at temperatures over 120°. This silicate is subsequently decomposed by hydrochloric acid, with the separation of silica. It is not, therefore, possible to separate all the silica by the evaporation of magnesian clays if the residue be dried at temperatures over 120°. A certain amount of soluble silica will always be formed by the decomposition of the resulting magnesian silicate. If magnesium be absent, the drying of calcareous silicates can be conducted at a higher temperature than 110°—for instance, 280°—when "it would seem that there is no tendency for silica to recombine with lime and alumina" (Gilbert).[2]

So long as any silica escapes transformation into the insoluble condition, so long will a certain proportion pass into solution, probably as sodium silicate, by the reaction between the sodium chloride and silicic acid. In illustration, Mr A. B. Trickett mixed Kahlbaum's "Kieselsäure"—silicic acid—with different proportions of sodium chloride solution (25 c.c. of the solution contained 5 grms.); evaporated the mixture to dryness, and baked the residue four hours in a steam oven. The insoluble silica was filtered off, washed, and the soluble silica determined in the filtrate by the molybdate colorimetric process (page 605).

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[1] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, 24. 262, 1904.

[2] If zinc be present, see page 359.

Table XXXI.—Effect of Sodium Chloride on "Soluble" Silica.

NaCl per gram SiO_2 (grms.).	SiO_2 in the filtrate (per cent.).
18·5	0·78
26·9	0·81
45·8	1·06
62·4	1·07

This shows that the greater the amount of sodium chloride in the solution, the greater the amount of silica in the filtrate, presumably owing to the transformation of silicic acid into soluble sodium silicate.

This re-solution of sodium silicate is one of the troubles attending the determination of silica. If the silicic acids could be completely dehydrated with baking below the temperature of recombination, the difficulty would be overcome. It is important to remove as much silica as possible at this stage of the analysis, since any silica which escapes in the filtrate will contaminate the different precipitates later on.[1] The possibility of a *recombination of the silica with the bases during the baking of the silica limits the safe temperature of desiccation.*[2] The complete drying, that is, the complete conversion of the silica into the insoluble form, might possibly be effected at 110° if an indefinite period of time were available. The longer the time of baking, the more perfect the drying, and the less the amount of silica which passes into solution in the filtrate. This is illustrated by the following experiments due to Hillebrand :—

Table XXXII.—Effect of Time of Drying on the "Soluble" Silica.

Time drying in steam oven (hours).	Silica in filtrate (per cent.).
4	2·11
24	1·63
48	1·48

In agreement with fig. 97, it follows that the complete "dehydration" of the silicic acid is excessively slow—too slow to be of any practical use.[3] It will therefore be obvious that taking up the dry residue with hydrochloric acid and re-drying the residue a number of times has very little influence on the "silica in filtrate." But if the silica which has separated be removed, the amount of silica remaining when the filtrate is evaporated to dryness is comparatively small. The drying curve for this silica resembles that indicated in fig. 97 ; and although a similar percentage of the silica will remain untransformed at the end of a certain period of drying, yet the actual amount is small in comparison with the total silica. Indeed, after the second evaporation and drying, less than 0·1 per cent. of the total silica will be found in the filtrate. This is very well illustrated by the following numbers :—

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[1] R. Bunsen, *Liebig's Ann.*, **61.** 265, 1847 ; E. Ludwig, *Pogg. Ann.*, **141.** 149, 1870 ; *Zeit. anal. Chem.*, **9.** 321, 1870 ; C. Meineke, *Rep. anal. Chem.*, **7.** 214, 1887 ; A. Cameron, *Chem. News*, **69.** 171, 1894 ; E. Jordis and W. Ludewig, *Zeit. anorg. Chem.*, **45.** 362, 1905 ; **47.** 180, 1905 ; N. Knight and F. A. Menneke, *Chem. News*, **94.** 165, 1906 ; J. A. Phillips, *Phil. Mag.* (4), **41.** 87, 1871.

[2] B. Blount, *Journ. Amer. Chem. Soc.*, **26.** 995, 1904. W. H. Stanger and B. Blount (*Journ. Soc. Chem. Ind.*, **21.** 1216, 1902) consider the temperature of baking Portland cements should not be lower than 200°. This high temperature is not safe for general work, although with calcareous cements, under industrial conditions, the results are satisfactory (Table XXVIII.). T. Bauer, *Tonind. Ztg.*, **37.** 89, 1913.

[3] It is probable that some volatile reagent—say alcohol, page 169—might be found to do the work efficiently, but this has not yet been fully investigated.

Filtrate	First.	Second.	Third.	Fourth.
Silica	0·00141	0·00081	0·00023	0·00006 grm.
Silica	0·0307	0·0035	0·0024	0·0015 grm.

Cameron gives the third evaporation, thus reducing the percentage silica in the third filtrate to a negligibly small amount, and after the fourth evaporation, the amount escaping dehydration is almost out of range of the balance.[1] Two evaporations suffice for technical work.

It follows from Table XXIX. that when the silicate under investigation is soluble, or almost wholly soluble in acid, say hydrochloric acid, and, in consequence, comparatively little sodium salt is present, one evaporation will be almost as effective as two. This explains how some discordant statements are rife. For instance, with Portland cement, which is nearly all soluble in hydrochloric acid, one evaporation and baking at 180° will suffice. The relatively large proportion of lime in these silicates also facilitates the dehydration of the silica, as indicated in Table XXIX., p. 174.[2]

Evaporation with sulphuric acid,[3] in place of hydrochloric acid, gives a silica which is comparatively easily dehydrated ;[4] but the presence of this acid is a source of danger on account of the risk of forming sparingly soluble sulphates which may contaminate the silica, and the escape of alumina from precipitation in the presence of sulphates—page 180.

The rate at which the silicic acid is dehydrated is connected with the concentration of the solution from which the silicic acid was precipitated by the hydrochloric acid. For instance, Mr J. C. Green has measured the amount of water driven off from silicic acid precipitated from concentrated and from dilute solutions of sodium silicate, and afterwards dried by heating up to 450°. His results are :—

Table XXXIII.—Dehydration of Silicic Acid at 800°.

Time heated at 800°. Minutes.	Amount of moisture lost—per cent.	
	Silica from concentrated solutions.	Silica from dilute solutions.
5	1·6	4·49
10	4·25	6·45
20	5·72	8·72
30	6·18	10·04

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[1] In these experiments the residues were not baked above 110°.

[2] B. Blount, *Journ. Amer. Chem. Soc.*, **26**. 995, 1904 ; S. F. Peckham, *ib.*, **26**. 1636, 1904.

[3] T. N. Drown, *Chem. News*, **40**. 40, 1879 ; *Trans. Amer. Inst. Min. Eng.*, **7**. 346, 1879 ; T. N. Drown and P. W. Shimer, *ib.*, **8**. 508, 1880 ; *Chem. News*, **42**. 299, 1880 ; J. Thill, *Zeit. anal. Chem.*, **43**. 552, 1904 ; G. H. Meeker, *Journ. Amer. Chem. Soc.*, **19**. 370, 1897 ; A. Cameron, *Chem. News*, **69**. 674, 1894 ; C. Craig, *ib.*, **60**. 227, 1889 ; J. P. Gilbert, *ib.*, **61**. 270, 281, 1890. V. M. Goldschmidt (*Tids. Kemie Pharm. Terap.*, 325, 1910) recommends making the silica insoluble by evaporation with nitric acid and hydrogen peroxide instead of with hydrochloric acid.

[4] Nitric acid is used in special cases—for instance, when lead is present.

CHAPTER XIII.

THE AMMONIA PRECIPITATE.

§ 85. The Precipitation by Means of Ammonia.

We have now to deal with the filtrate, acidified with hydrochloric acid, from the silica. This solution contains aluminium, iron, titanium, phosphorus, manganese, calcium, magnesium, and alkaline salts.[1] Assume that the manganese is either absent, or present in inappreciable quantities.[2] The addition of ammonia, in the presence of ammonium chloride,[3] precipitates the aluminium, iron,[4] phosphorus, titanium,[5] and part of the magnesium. The precipitate carries down a little lime and alkalies.[6] The ammonia should be added drop by drop with constant stirring. "If an excess of ammonia be poured into the solution rather quickly, a considerable quantity of magnesia will be precipitated with the alumina"; whereas, "if the ammonia be added, drop by drop, with constant stirring, to the hot solution, until the ammonia is in slight excess, the precipitated alumina will be either free from magnesia, or retain but slight traces of that element."[1] In illustration, mixtures of 1·23 grms. of magnesium sulphate, with 2·2675 grms. of ammonia alum with 10 grms. of ammonium chloride in 750 c.c. of boiling water, gave precipitates which weighed, after ignition—

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[1] If lead, bismuth, copper, cadmium, tin, arsenic, molybdenum, antimony, selenium, gold, and the platinum metals be present, they should be removed by hydrogen sulphide, etc. as indicated later on page 186.

[2] If manganese be present, and time is of great importance, add a few cubic centimetres of bromine water, or a few drops of bromine (page 372) to the boiling solution containing the equivalent of 10 per cent. of concentrated hydrochloric acid by volume. Make the solution alkaline with ammonia, or add hydrogen peroxide with the ammonium chloride and ammonia—M. Dittrich, *Ber.*, **35**. 4072, 1902. The manganese will be precipitated with the alumina, iron, etc. The presence of one part of iron in 80,000 parts of solution gives a visible precipitate with aqueous ammonia; for aluminium the numbers are 1—100,000; for chromium, 1—170,000; zinc, 1—80,000; manganese, 1—170,000.—L. J. Curtmann and A. D. St John, *Journ. Amer. Chem. Soc.*, **34**. 1679, 1912.

[3] A. Mitscherlich, *Journ. prakt. Chem.* (1), **81**. 108, 1860; (1), **83**. 458, 1861.

[4] Ferric, not ferrous oxide. But the iron after the preceding treatment will generally be all ferric. If much manganese be present (as will be indicated by the colour of the sodium carbonate fusion), the filtrate from the silica may contain ferrous iron. "The tendency of manganese salts to exert a reducing effect on ferric iron in solution is probably the cause of this phenomenon"—G. C. Stone (W. G. Waring, *Journ. Amer. Chem. Soc.*, **26**. 4, 1904). If ferrous salts be present, a few drops of hydrogen peroxide will effect the conversion (A. Carnot, *Compt. Rend.*, **107**. 948, 997, 1888). If hydrogen sulphide has been employed to remove the metals indicated in a preceding footnote, it will be necessary to remove the hydrogen sulphide by boiling, filter off the sulphur, and oxidise the iron. Note that commercial hydrogen peroxide sometimes contains fluorine, chlorine, sulphuric acid, hydrofluosilicic acid, sugar, glycerine, calcium, magnesium, barium and aluminium salts, etc.—H. P. Talbot and H. R. Moody, *Tech. Quart.*, **5**. 123, 1893; G. Arth, *Monit. Scient.* (4), **15**. 715, 1901; *Chem. News*, **85**. 184, 1902. To purify the hydrogen peroxide: (1) Add one-tenth the volume of alcohol; add powdered barium hydroxide free from carbonate; filter on the pump; precipitate barium with a slight excess of sulphuric acid; evaporate off the alcohol. (2) Precipitate the silica and hydrofluosilicic acid with potash lye; filter; and distil under reduced pressure. See page 205.

[5] If chromium, beryllium, vanadium, and the rare earths be present, they too will be precipitated as hydroxides; uranium will be precipitated as ammonium diuranate—$(NH_4)_2U_2O_7$.

[6] C. F. Cross, *Proc. Manchester Lit. Phil. Soc.*, **17**. 49, 1877; P. Cornette, *Ann. Pharm.*, **4**. 1, 1900; J. Thoulet, *Compt. Rend.*, **99**. 1072, 1884; R. Warrington, *Journ. Chem. Soc.*, **21**. 1, 1868. Some consider that the precipitated hydroxide forms a true chemical compound with the substances in question. *E.g.*, A. V. E. Young, *Amer. Chem. Journ.*, **8**. 23, 1886 (Al); V. J. Hall, *ib.*, **19**. 512, 1897 (Fe); **19**. 901, 1897 (Zn); H. P. Patten, *ib.*, **18**. 608, 1896 (Cr); *Journ. Amer. Chem. Soc.*, **25**. 186, 1903 (Mg, Mn, $BaSO_4$).

Slow precipitation . . .	0·2581	0·4910 grm.
Rapid precipitation . . .	0·2641	0·4965 grm.

The precipitate should be dissolved in hot hydrochloric acid, and reprecipitated, washed, ignited, and weighed. The ignited mass is then fused with potassium pyrosulphate, and the resulting cake digested with water. The insoluble silica[2] is filtered off, washed, and weighed as "extra silica." The iron, titanium, phosphorus, and manganese, if present in the filtrate, are determined separately. The amounts of these constituents are added together, and the difference between the sum and the weight of the total ammonia precipitate is the alumina. Before taking up details of the process, a few special points may be considered.

Ammonia for the "Alumina" Precipitation.—The ammonia used should be free from carbonates; otherwise, calcium carbonate will be precipitated with the alumina, etc.[3] Ammonia[4] absorbs carbon dioxide from the atmosphere, and hence some analysts make a fresh solution of ammonia periodically for this work. If calcium carbonate be formed, H. Rose[5] thinks that it will be decomposed by the ammonium salts present in the solution, when the mixture is boiled. The ammonia should be kept in cerasine bottles, or glass bottles lined on the inside with cerasine. Freshly prepared ammonia kept in common glass bottles for one month gave a residue of 0·7 grm. per 25 c.c.; in a Jena glass bottle, 0·4 grm.; and in cerasine bottles, no residue.[6]

Influence of Boiling and Long Standing on the Alumina Precipitate.—There are some objections to the boiling of solutions containing the alumina precipitate. Rose and Fresenius[7] recommend boiling off the excess of ammonia from the solution. Lunge[8] considers the boiling unnecessary. The objections to the boiling are: (1) Some alumina may be redissolved by prolonged boiling owing to the decomposition of the ammonium chloride, with the formation of hydrochloric acid and volatile ammonia.[9] Hence, it is well to make sure that the solution is alkaline before filtering. (2) Prolonged boiling to drive off the excess of ammonia may lead to a contamination of the precipitate by dissolution of silica, etc., from the glass vessels. (3) Prolonged boiling also tends to make the precipitate slimy and difficult to filter and wash. The same objection applies to precipitates which have stood some time. (4) Calcium carbonate is also precipitated under these conditions owing to the absorption of carbon dioxide from the air.

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[1] L. F. J. Wrinkle, *Chem. News*, **22.** 4, 1870; H. Abich, *Pogg. Ann.*, **23.** 352, 1831; W. R Nichols, *Amer. J. Science* (2), **47.** 16, 1869.

[2] The trace which escapes in the second filtrate mentioned in the preceding chapter, as well as any dissolved from the glass vessels, reagents, etc., will be, for the most part, recovered later.

[3] For the action of ammonia on silica, see pages 172 and 183.

[4] The ammonia is tested for carbon dioxide by an aqueous solution of calcium chloride. There should be no opalescence. For the analysis of commercial "aqua ammonia," see J. D. Pennock and D. A. Morton, *Journ. Amer. Chem. Soc.*, **24.** 377, 1902. For pyridine in ammonia, see H. Ost, *Journ. prakt. Chem.* (2), **28.** 271, 1883; for lead, see W. F. Lowe, *Journ. Soc. Chem. Ind.*, **11.** 133, 1892. The latter impurity is introduced when the manufacturer places the ammonia in leaden vessels for dilution to the required specific gravity.

[5] H. Rose, *Chem. News*, **2.** 291, 1860; *Pogg. Ann.*, **110.** 292, 1860.

[6] E. T. Allen and J. Johnston, *Journ. Ind. Eng. Chem.*, **2.** 196, 1910.

[7] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1.** 160, 1903; London, **1.** 192, 1900; L. Blum, *Zeit. anal. Chem.*, **27.** 19, 1888; H. Rose, *l.c.* For the action of ammonium chloride on metallic sulphides, see P. de Clermont, *Compt. Rend.*, **88.** 972, 1879.

[8] G. Lunge, *Zeit. angew. Chem.*, **12.** 635, 1889; G. Lunge and H. von Kéler, **7.** 670, 1894; C. Meineke, *Rep. anal. Chem.*, **7.** 214, 757, 1888.

[9] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2.** 807, 1905; R. Fittig, *Zeit. anal. Chem.*, **27.** 29, 1888; *Liebig's Ann.*, **128.** 189, 1863; H. C. Dibbits, *Zeit. anal. Chem.*, **15.** 245, 1876; *Ber.*, **5.** 820, 1872; A. R. Leeds, *Chem. News*, **29.** 256, 1874; D. Gernez, *Compt. Rend.*, **64.** 606, 1867.

The important thing is to filter rapidly. If the filtration and washing of the precipitate from a gram of clay occupy much over half an hour, it will be almost impossible to remove the adsorbed salts, in a reasonable time, by washing—hence some use a hot funnel (fig. 130). If the precipitate has reached the slimy stage[1] before the washing is completed, it is generally advisable to redissolve it in hydrochloric acid, and reprecipitate. For the reasons stated above, if the filtrate from the silica has to be left standing some days, let the solution be acidified by hydrochloric acid before "shelving." Do not let the alumina precipitate stand in its mother liquid unfiltered.

The effect of temperature, etc., on the precipitation of colloids, of which the ammonia precipitate is a typical example, has been discussed on page 96.

Filtration of Gelatinous Precipitates.—Before adding the ammonia, Dittrich[2] mixes the solution with macerated filter paper pulp.[3] This facilitates the washing of the gelatinous precipitate, and also the oxidation of the precipitate during the ignition. The process gives good results. The precipitate is rather bulky, and accordingly a larger filter paper must be used, and also a larger crucible for the ignition. A certain amount of salt is absorbed by the filter paper, although Mansier[4] says that sodium chloride is not retained by the washed paper. Do not use paper pulp for highly ferruginous clays, for reasons which will appear later (page 184).

In order to coagulate gelatinous precipitates, and render them easy to filter, Divine,[5] recommends the addition of 6 c.c. of a 2·5 per cent. solution of tannin—the addition of 2 c.c. of the tannin solution, before adding the ammonia, works well. Guyard[6] recommended the addition of glycerol; Palmer, stirring with one or two drops of albumen (white of egg), and heating to boiling; Liebermann uses starch in a similar manner; Warren, a few drops of an ethereal solution of pyroxyline; and Zulkowsky recommended shaking the liquid with one-third of its volume of ether. The ether entangles the precipitate and carries it to the surface. Some of these recommendations must be adopted with caution, on account of the tendency of organic substances to retard the precipitation of alumina. Glycerol, for instance, is under certain conditions highly objectionable.[1]

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[1] The precipitated aluminium and ferric hydroxides sometimes appear to dissolve and pass through the filter paper, particularly towards the end of a washing—C. F. Cross, *Chem. News*, **39**. 161, 1879; E. Schirm, *Collegium*, 99, 1911. G. P. Baxter and R. A. Hubbard (*Journ. Amer. Chem. Soc.*, **28**. 1208, 1906) state "that the solubility of ferric oxide in ammonia is caused by the presence of some organic impurity in the ammonia," and they tried, without success, to reproduce the phenomenon by mixing methyl-, ethyl-, diethyl-, isoamyl-amines, ethylenediamine, aniline, and phenylhydrazine with the ammonia. I have always attributed the phenomenon to a deflocculation of the colloidal precipitate (page 96).

[2] H. Jervis, *Chem. News*, **78**. 257, 1898; F. Ibbotson, *Technics*, **2**. 357, 1904; M. Dittrich, *Ber.*, **37**. 1840, 1904. A. C. F. M'Kenna (*Jour. Amer. Chem. Soc.*, **21**. 125, 1899; *Chem. News*, **79**. 184, 1899) recommended the paper pulp process for zinc sulphide in 1899; E. Murmann (*Zeit. anal. Chem.*, **50**. 742, 1911) recommends the addition of a little of the finest starch, mercuric sulphide, or shredded paper for gelatinous precipitates like aluminium hydroxide, manganese and zinc sulphides, etc.

[3] Paper Pulp for Filtration.—The pulp may be prepared for filtration in the following manner:—Crush Swedish filter paper into small balls, put the balls into a large empty cerasine bottle. Add concentrated hydrochloric acid, and a little hydrofluoric acid. Seal up the stopper of the bottle with wax, and shake in a shaking machine for a couple of hours. Wash the resulting pulp free from acid by decantation. Keep the emulsion of pulp and water in a bottle for use.

[4] M. Mansier, *Rev. Internat. Falsif.*, **15**. 115, 1903.

[5] R. E. Divine, *Journ. Soc. Chem. Ind.*, **24**. 11, 1905.

[6] A. Guyard, *Zeit. anal. Chem.*, **22**. 426, 1883; L. Liebermann, *ib.*, **14**. 359, 1875; K. Zulkowsky, *Chem. Ztg.*, **8**. 772, 1885; H. N. Warren, *Chem. News*, **61**. 63, 1890; C. S. Palmer, *Eng. Min. Journ.*, **80**. 582, 1906. T. M. Chatard (*Amer. J. Science* (2), **50**. 247, 1870; (3), **2**. 416, 1871; *Chem. News*, **22**. 246, 1870; **24**. 270, 1871) recommends the evaporation of gelatinous precipitates to dryness on a water bath, when it is claimed that chromic, ferric, aluminium, beryllium, titanium hydroxides; nickel carbonate; cerium, lanthanium, and didymium oxalates become granular and easy to filter. The washing of these precipitates free from salts is then a difficulty.

Influence of Fluorides on the Precipitation of Alumina.—The presence of fluorides hinders the precipitation of aluminium hydroxide by ammonia.[2] A soluble aluminium fluoride is produced which is not completely decomposed by the ammonia. The reaction is represented by the equation :

$$AlF_3 + 3NH_4OH \rightleftharpoons Al(OH)_3 + 3NH_4F.$$

The reaction therefore proceeds in both directions, and in all probability a soluble salt, $(NH_4)_3AlF_6$, is produced when much ammonium fluoride is present. The effect of different proportions of ammonium fluoride on the amount of alumina which is "lost," owing to its remaining in solution, is shown by the graph, fig. 98. This was worked out by Hinrichsen. Hinrichsen further showed the danger of introducing fluorine into the solution when the clays, etc., are opened up with sulphuric and hydrofluoric acids, and when the silica is corrected by treatment with the same acids, because of the difficulty in driving off the last traces of the fluorine. In these cases the solution should be evaporated to dryness, and the residue calcined in order to transform the fluorides into oxides. There is then no difficulty with the fluorine.

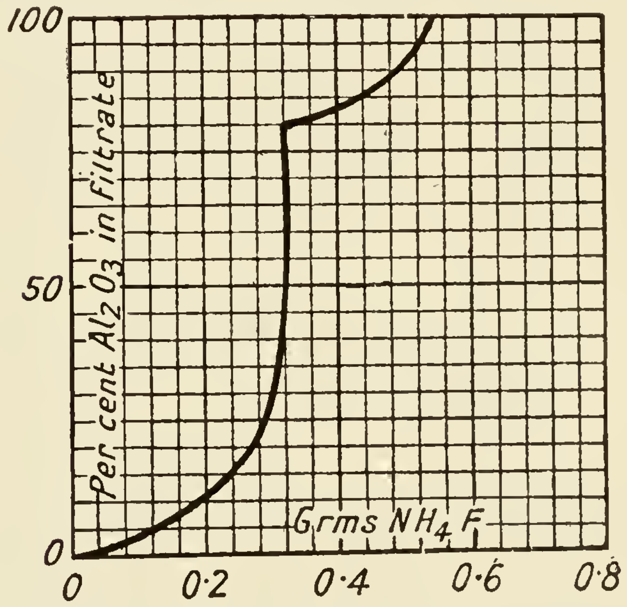

FIG. 98.—Action of fluorides on the precipitation of alumina (Hinrichsen).

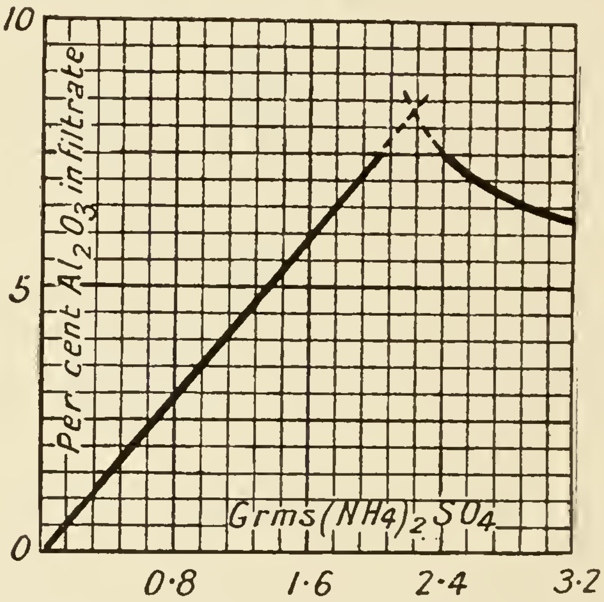

FIG. 99.—Action of sulphates on the precipitation of alumina (Trickett).

Influence of Sulphates on the Precipitation of Alumina.—There is also a risk of alumina escaping precipitation in the presence of sulphates. Mr A. B. Trickett, in my laboratory, has measured the amount of alumina which escapes precipitation in the presence of different amounts of ammonium sulphate, and his results are illustrated by the graph, fig. 99. Starting with the equivalent of 0·0077 grm. of Al_2O_3 in solution, and increasing the amount of ammonium sulphate from 0·8 to 3·2 grms. (abscissæ, fig. 99), the corresponding amounts of alumina in solution when an excess of ammonia is added are represented in the diagram.

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[1] A. Guyard, *Bull. Soc. Chim.* (2), **31**. 354, 1879.

[2] F. P. Veitch, *Journ. Amer. Chem. Soc.*, **22**. 246, 1900 ; W. R. Bloor, *ib.*, **29**. 1603, 1907 ; L. J. Curtman and H. Dubin, *ib.*, **34**. 1485, 1912 ; F. W. Hinrichsen, *Ber.*, **40**. 1497, 1907 ; *Zeit. anorg. Chem.*, **58**. 83, 1908.

The presence of a large excess of ammonium chloride appears to reduce the amount of alumina which escapes precipitation in this manner.

According to Wrinkle,[1] magnesia is much more liable to be precipitated with the alumina if sulphates be present.

§ 86. The Theory of the Ammonia Precipitation.

Many salt solutions are decomposed by the action of water. The phenomenon is termed **hydrolysis**. Thus, bismuth or antimony chlorides with water form insoluble oxychlorides; mercuric sulphate forms a basic sulphate; and boiling solutions of ferric chloride form a mixture of ferric hydroxide and a basic ferric chloride, together with free hydrochloric acid. It is possible to draw up a list of salts where the phenomenon is marked and well-defined at one end of the series, and at the other end the hydrolysis is but ill-defined and feeble. In the former case the reaction is quantitative, and may be employed in analytical separations; in the latter case the separations are incomplete.

It will be observed that an acid is usually one product of the hydrolysis. For instance, the hydrolysis of titanic sulphate is represented in symbols—

$$Ti(SO_4)_2 + 4H_2O \rightleftharpoons 2H_2SO_4 + Ti(OH)_4.$$

Titanium hydroxide—$Ti(OH)_4$—is soluble in the free acid, but at first the rate at which the sulphate is decomposed is much greater than the rate of dissolution of the hydroxide by the acid. Hence, acid accumulates in the solution. As the acid accumulates in the solution, its effects become more and more marked, and finally, when the free acid has attained a certain concentration, the speeds of the two reactions will be equal, and no further separation of the hydroxide will be observed, because it will be dissolved by the free acid as fast as it is formed.

When weak bases—aniline, ammonia, phenylhydrazine, etc.—are present, some of the liberated acid is converted into a neutral salt of the base. The concentration of the free acid is thus diminished, and a much greater proportion of the hydroxide will separate. If a sufficient quantity of the base be present to prevent the acid accumulating in the system, all the salt may be hydrolysed.

The salt—say, ammonium chloride, NH_4Cl—formed by the union of the base with the free acid may itself be hydrolysed by the water—

$$H_2O + NH_4Cl \rightleftharpoons NH_4OH + HCl.$$

Hence, there is a limit to the work the base can do in neutralising the free acid. In the case of the alumina precipitation, there is nearly always enough free acid present to prevent the hydrolysis of the magnesium salts, whereas with aluminium, titanium, zirconium, chromium, beryllium, thorium, cerium, and ferric salts, the liberated hydroxide can exist in the presence of the small amount of free acid produced by the hydrolysis of the ammonium salt.

The complete separation of these hydroxides thus depends upon the amount of free acid which is liberated by the hydrolysis of the salt formed by the combination of the freed acid with the base. With aniline more free acid will be formed in the system than with phenylhydrazine, and with phenylhydrazine, more than with ammonia. Hence, hydroxides completely precipitated by ammonia may be only partially precipitated by phenylhydrazine, and not at all by aniline. With beryllium chloride, for example, the hydroxide is completely precipitated by phenylhydrazine, but not by aniline, and ferric iron is precipitated by ammonia, but not by phenylhydrazine. The nature of the acid is of great importance, since the salts of one acid may be more susceptible to hydrolysis than the salts of another. Thus, complete precipitation may occur with beryllium chloride, while but a trace is precipitated with the nitrate.[1]

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[1] L. F. J. Wrinkle, *Chem. News*, **22**. 4, 1870. According to H. Bley (*Journ. prakt. Chem.* (1), **39**. 1, 1846), a certain amount of sulphuric acid or sulphate may also be dragged down with the precipitate.

The general principle here indicated may, of course, be modified in special cases, because of the formation of double salts, basic salts, etc.

Some authors attribute the effect of ammonium salts, in retarding the precipitation of magnesium hydroxide by ammonia, to the formation of the complex salt—$Mg(NH_4)_2Cl_4$—which is not decomposed by ammonia. As a matter of fact, ammonia, in the absence of ammonium salts, precipitates half the magnesium as hydroxide, and the other half as the complex salt. It is then supposed that the addition of an ammonium salt dissolves the hydroxide with the formation of more $Mg(NH_4)_2Cl_4$. The accumulation of ammonium chloride[2] in the system will also lessen the amount of the hydrolysed salt in accord with the view indicated in the text.[3] Similar remarks might be applied to manganese salts. With zinc,[4] cobalt,[5] and nickel[6] complex salts may be formed, so that both influences indicated above come into play.

§ 87. The Determination of the Ammonia Precipitate.

First Precipitation.—The filtrate from the silica, in a 400-c.c. beaker, is mixed with about 10 c.c. of ammonium chloride solution[7] and heated to boiling.[8] Aqueous ammonia is then added in slight excess.[9] The ammonia is added slowly in order to prevent bubbles of gas violently projecting some of the hot liquid from the beaker. While the solution is still boiling, filter promptly through, say, a 12·5-cm. filter paper,[1] and wash four times by decantation[2] with a hot solution of ammonium nitrate[3] in order to coagulate the gelatinous precipitate. The filter paper is washed at the same time.

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[1] A. M. Jefferson, *Journ. Amer. Chem. Soc.*, **24.** 540, 1902; B. L. Hartwell, *ib.*, **25.** 1128, 1903; E. T. Allen, *ib.*, **25.** 421, 1903; W. H. Hess and E. D. Campbell, *ib.*, **21.** 776, 1889.

[2] J. M. Lovén, *Zeit. anorg. Chem.*, **11.** 404, 1896; F. P. Treadwell, *ib.*, **37.** 326, 1904; W. Herz and G. Muhs, *ib.*, **38.** 138, 1904.

[3] Usually the solution contains sufficient hydrochloric acid to form enough ammonium chloride with the ammonia to prevent the precipitation of the magnesium hydroxide. A. A. Noyes, W. C. Bray, and E. B. Spears (*Tech. Quart.*, **21.** 14, 1908; *Journ. Amer. Chem. Soc.*, **30.** 481, 1908) state that 0·005 grm. of magnesium chloride made up with 5 c.c. of hydrochloric acid (sp. gr. 1·12) to 100 c.c. gave no precipitate with 40 c.c. of ammonia (sp. gr. 0·96), but a precipitate appeared with 50 c.c. of ammonia.

[4] W. Herz, *Zeit. anorg. Chem.*, **25.** 225, 1900; W. Gaus, *ib.*, **25.** 236, 1900; W. Bonsdorff, *ib.*, **41.** 132, 1904; H. Euler, *Ber.*, **36.** 3400, 1903.

[5] A. Werner, *Ber.*, **40.** 15, 1907.

[6] H. M. Dawson and J. M'Crae, *Journ. Chem. Soc.*, **77.** 1239, 1900; W. Bonsdorff, *Zeit. anorg. Chem.*, **41.** 132, 1904; M. Konowaloff, *Chem. Centr.*, i. 646, 1900.

[7] Ammonium Chloride Solution.—107 grms. of the salt per litre. The object of the ammonium chloride is to retard the precipitation of magnesium and manganese hydroxides, as indicated above.

[8] W. E. Taylor (*Chem. News*, **103.** 169, 1911) claims that adding the ammonia to the solution at 66°, and then raising the temperature to the boiling point, gives a more granular precipitate than adding ammonia to the boiling solution.

[9] The use of the term "excess" in analytical chemistry often misleads beginners. It is comparatively rare to find reactions in which complete precipitation is effected by adding the theoretical amount of the precipitating agent. When such reactions are known, they generally make useful volumetric processes. In most cases, more of the precipitating agent must be added than is satisfied by the regular type of equation representing the reaction. *The term "excess" means that enough precipitating agent must be added to ensure complete precipitation—and no more.* As J. W. Mallet used to say, *ad maxima per minima.* Analytical chemistry has not yet reached that stage where it can answer, for each reaction, the following types of question: What amount constitutes an excess? How does this excess differ when different salts are present? Does the presence of certain salts diminish the amount of the "excess" needed? etc.

Second Precipitation.—Hot dilute hydrochloric acid (1 : 1) is then run through the filter paper into the beaker in which the precipitation was first made. The precipitate dissolves.[4] The precipitation with ammonium chloride and ammonia is repeated. The precipitate is washed as before four times by decantation, with a hot solution of ammonium nitrate. The precipitate is then transferred to the filter paper,[5] and washed with the hot solution of ammonium nitrate until the washing liquid is free from chlorides, when a few drops of the filtrate are tested with silver nitrate.

Recovery of Alumina and Silica from the Filtrate.—Towards the end of the washing, a re-solution of some of the alumina precipitate sometimes takes place.[6] In any case some alumina and silica[7] is generally found in the filtrate. This must be recovered. Evaporate the filtrate nearly to dryness.[8] Ammonia is added to the solution and the evaporation continued. The solution is kept alkaline to coagulate any iron and aluminium hydroxides. Collect and wash these on a 5-cm. filter paper, and run the filtrate in, say, a 250-c.c. beaker. The filtrate is used for the determination of lime and magnesia.[9]

Ignition of the Precipitate.—Let the precipitate drain, and transfer the filter paper and contents, while still moist, to the platinum crucible containing the residue from the silica. Put the filter paper[10] in the crucible with the triple fold uppermost, and leave a passage for the exit of steam.[1] Ignite the precipitate, slowly at first, in order to prevent the bubbling mass from carrying a portion of the precipitate to the upper side of the crucible, where it is liable to stick, and subsequently escape the solvent action of the potassium pyrosulphate. Heat the crucible until the paper is charred. The crucible[2] is of course laid on its side on the platinum triangle to permit free access of air, and heated red-hot about 20 minutes. This is followed by 5 to 10 minutes' blasting, or heating over a Méker's burner. The alumina is not properly dehydrated if heated on the ordinary Bunsen's burner.[3] Let the crucible cool in a desiccator. Moisten the cold mass with a drop of concentrated nitric acid, and heat gently until no more fumes are evolved. Re-ignite, cool, and weigh. The number remaining when the weight of the empty crucible has been subtracted, gives the weight of the alumina, ferric oxide,[4] titanic oxide, and phosphoric oxide (if present) in the precipitate.[5]

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[1] With many clays the precipitate settles too slowly for washing by decantation.

[2] For china clays use a 12·5-cm. paper ; for Cornish stone, a 11-cm. paper ; and for glazes and siliceous clays, a 9-cm. or even a 7-cm. paper will be ample ; see page 89.

[3] Ammonium Nitrate Solution.—Neutralise 20 c.c. of concentrated nitric acid with ammonia, and dilute to a litre (R. Bunsen, *Liebig's Ann.*, **106**. 13, 1858 ; S. L. Penfield and D. N. Harper, *Amer. J. Science* (3), **32**. 112, 1886 ; *Chem. News*, **54**. 90, 102, 1886). A few drops of litmus will indicate whether the solution be acid. An acid solution is, of course, fatal to success.

[4] Freshly precipitated aluminium and ferric hydroxides are readily soluble in dilute acids, but after standing a short time they take a long time to dissolve—M. Jeannel, *Compt. Rend.*, **66**. 799, 1868 ; J. Attfield, *Chem. News*, **17**. 303, 1868. Hence the need for speedy work. To facilitate the solution of gelatinous precipitates, F. A. Gooch (*Zeit. anorg. Chem.*, **46**. 208, 1906 ; *Chem. News*, **92**. 64, 1905) uses a cone of platinum gauze between the filter paper and the precipitate. Most of the precipitate can then be lifted with the cone from the paper and transferred to the beaker for solution—P. T. Austen, *Chem. News*, **38**. 88, 1878.

[5] Instead of the "policeman," a swab made from a quarter of a 7-cm. paper may be rubbed against the sides of the beaker and transferred to the filter paper. The swabbing is repeated with each of the other three quarters.

[6] When water alone is used for the washing, or the ammonium nitrate solution becomes acid.

[7] For the solubility of silica in aqueous ammonia, and water, see W. Skey, *Chem. News*, **17**. 165, 1868 ; A. M. Edwards, *ib.*, **73**. 13, 1896 ; R. Pribram, *Wittstein's Viertel.*, **16**. 30, 1867 ; *Chem. News*, **17**. 227, 1868 ; A. Souchay, *Zeit. anal. Chem.*, **11**. 187, 1872 ; G. Karsten, *Pogg. Ann.*, **6**. 357, 1826.

[8] It is best to evaporate the main filtrate and washings separately. The washings are taken to dryness, and the ammonium salts driven off.

[9] F. Muck (*Zeit. anal. Chem.*, **19**. 140, 1880) recommends removing the sodium and potassium chlorides which accumulate in the solution—particularly after the "basic acetate separation" (page 362)—by evaporating the solution to dryness ; dissolving the residue in concentrated hydrochloric acid ; and washing the residual salts with concentrated acid on a glass-wool filter. There is, however, rarely any occasion for this operation. Ammonium salts are usually removed by evaporation to dryness and direct volatilisation, or by heating with nitric acid (H. Jervis, *Chem. News*, **86**. 271, 1902), or with some nitrous acid (P. Jannasch, *Journ. prakt. Chem.* (2), **72**. 38, 1905).

[10] Also the filter paper containing the residual alumina.

Dissolution of the Ignited Precipitate.—The precipitate dissolves so slowly in acids that it is advisable to fuse the ignited precipitate with about six times its weight of potassium pyrosulphate.[6] The preliminary heating, especially if potassium bisulphate be employed in place of the pyrosulphate, must be very gradual, in order to avoid loss by the spattering of the fused mass. The covered crucible is heated over a small flame until the contents are melted. The crucible is then raised six or nine inches above the flame, as illustrated in fig. 100. The moisture can then be driven off without danger. The crucible can be lowered nearer the flame in a short time.[1] If any particles of the precipitate adhere to the sides, wash them down by imparting a rotary motion to the contents of the crucible, or tilt the crucible a little to permit the fused salt to act on the grains. Slowly raise the temperature until the bottom of the crucible shows faint redness, but watch carefully to prevent frothing. If the crucible be lifted away with the tongs, and the contents of the cooling crucible be watched in a good light, it will be easy to see through the transparent mass if all has dissolved. Heat the crucible a few minutes more, even if all has dissolved.[2] Cool by placing the crucible on a cold slab. When cold, pour cold water into the crucible. The cake soon comes away from the crucible. It is then dissolved in water.[3] The cake dissolves quicker in warm water, but if the solution be boiled, titanium oxide may be precipitated. The solution is mixed with about 10 c.c. of dilute sulphuric acid. It is well to know how much acid and pyrosulphate have been employed, so that an allowance can be made later on when dealing with the titanium.

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[1] With highly ferruginous clays it is best to dry the precipitate in an air bath at about 110°, and ignite the paper separately in order to prevent the reduction of the ferric oxide by the carbon of the paper. The magnetic oxide of iron formed by the reduction cannot easily be reoxidised to Fe_2O_3, since it is protected from the air when buried in the alumina. Alumina, however, "decolorises" the ferric oxide and retards the reduction to magnetic oxide (H. Wartha, *Chem. News*, **84**. 305, 1901); indeed, a mixture of alumina with 6·8 per cent. of Fe_3O_4 after ignition contained nothing but ferric oxide. If the alumina has been precipitated with paper pulp, this precaution is not required, since the precipitate is then fine enough and open enough to readily reoxidise, even if it be partly reduced W. Suida (*Tschermak's Mitt.* (1), **5**. 176, 1876) has shown that calcined ferric oxide is not reduced to ferrous oxide if reducing agents be excluded (H. Rose, *Pharm. Centr.* (1), **19**. 483, 1848). C. Bodewig (*Zeit. Kryst.*, **7**. 176, 1883) states that there is always a certain amount of reduction in platinum crucibles, even when the crucible is but half covered with a sloping lid, since the ignited precipitate, when taken up with hydrochloric acid, gives a blue coloration with potassium ferricyanide. H. St C. Deville and L. Troost (*Compt. Rend.*, **56**. 977, 1863) have shown that platinum is permeable to the flame gases at high temperatures (see page 372). Bodewig prefers to ignite the precipitate in a porcelain crucible, moisten with nitric acid, dry, ignite, and weigh. This sequence of operations is repeated a second time. The oxide thus obtained is said to be free from ferrous oxide.

[2] H. von Jüptner (*Chem. Ztg.*, **13**. 1303, 1889) has devised a little asbestos cover for crucibles which accelerates the combustion of filter papers, and of organic matter during "ignitions."

[3] A. Mitscherlich, *Zeit. anal. Chem.*, **1**. 67, 1862; E. T. Allen and V. H. Gottschalk, *Amer. Chem. Journ.*, **24**. 292, 1900; E. T. Allen and H. F. Rogers, *ib.*, **24**. 304, 1900; but see page 173.

[4] Ferric oxide sometimes stains the platinum crucible badly (see page 115). This stain can generally be removed by letting the crucible stand overnight in contact with concentrated hydrochloric acid, and then warming it for a short time. Fused potassium bisulphate or pyrosulphate will also clean off the iron stain.

[5] Here, too, will be found, if present: niobium (columbium), tantalium, tungsten, zirconium, beryllium, chromium, thorium, and the rare earths. In the rare event of a determination of these constituents being required, see the later pages of this work.

[6] Some prefer potassium bisulphate, but with this salt the rise of temperature must be very, very gradual in order to prevent frothing over. This means an expenditure of time. The pyrosulphate gives less trouble in this respect. It is necessary to examine the commercially pure potassium pyrosulphate. I have found a number of packages of the best potassium pyrosulphate, sold by a celebrated maker of pure chemicals, containing bits of glass. This impurity is fatal to successful work. It is derived from the glass vessels in which the salt is fused. The glass vessels are broken to get the pyrosulphate out. To convert ordinary bisulphate to the pyrosulphate, melt the bisulphate in a platinum dish, and when the spluttering has ceased, and white fumes begin to come off freely, pour the fused mass on to another dish or plate. When cold, the pyrosulphate can be easily broken into pieces and bottled. J. L. Smith (*Amer. J. Science* (2), **40**. 248, 1865) preferred the sodium salt. It acts more rapidly than the potassium salt, and also forms a more suitable cake. It is, however, liable to crust over during

Correction for Silica.—The solution formed by the dissolution of the cake is evaporated on a water bath to a small volume and then heated to a higher temperature until fumes of sulphuric acid come off copiously.[4] Sufficient sulphuric acid should be present to form a pasty mass when the dish is cold. Water is added to the cold mass. The dish is placed on a water bath, and the silica which separates is filtered off, washed, ignited, and weighed.[5] The residue is treated with hydrofluoric acid, as indicated on page 169. The residue is ignited and weighed. The difference in the two weighings is called the "extra silica"; its weight is to be subtracted from the weight of the precipitate,

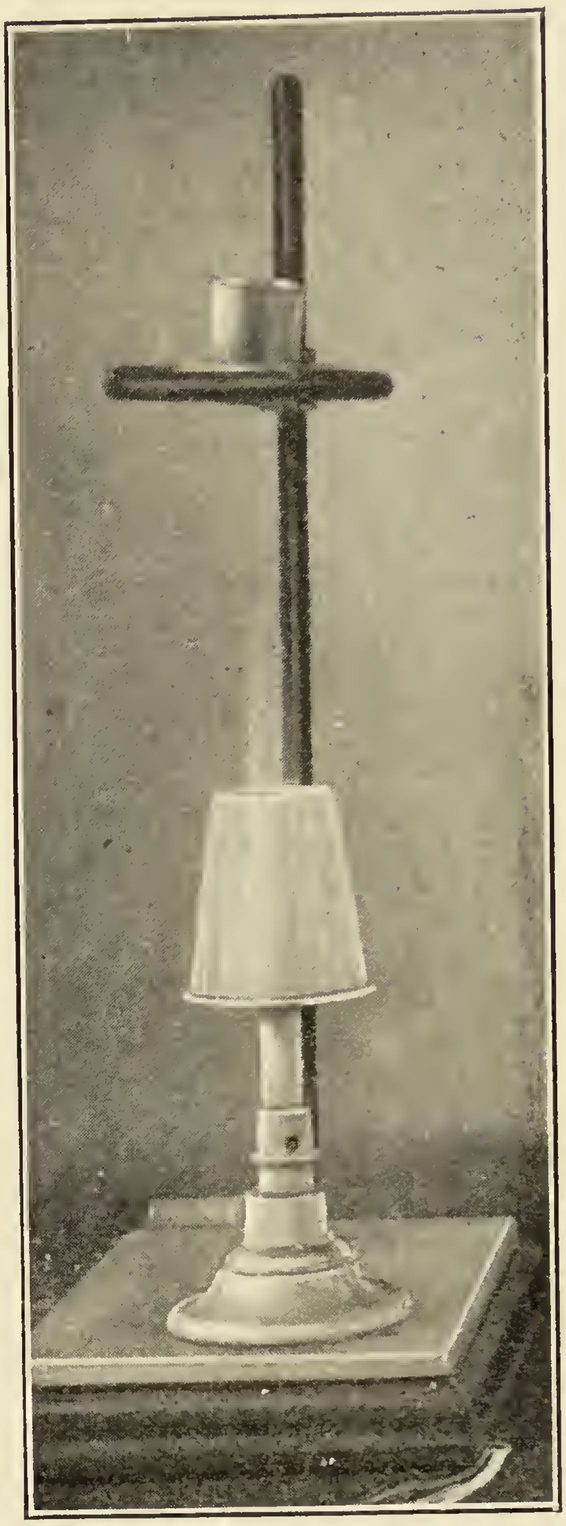

FIG. 100.—Pyrosulphate fusion.

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the fusion; and the cold cake is not so easily detached from the crucible as when potassium pyrosulphate is employed. It can be adopted with advantage. E. Deussen (*Zeit. anorg. Chem.*, 44. 423, 1905) recommended acid potassium fluoride with the idea of eliminating the solvent action of the pyrosulphate on the platinum. This salt is not to be recommended in accurate silicate analyses, because (1) the "extra silica" is lost; and (2) the fluorine, unless expelled, later on interferes with the permanganate titration and the titanium determination.

[1] Half an hour, if potassium bisulphate be used instead of the pyrosulphate.

[2] If the mass be heated too strongly and normal potassium sulphate be formed, the small contraction of the cooling sulphate and the relatively large contraction of the crucible may cause the crucible to burst.

[3] E. Hart (*Journ. Anal. App. Chem.*, 2. 410, 1888) adds concentrated sulphuric acid in excess, and warms the mixture until the mass is dissolved. When cold, dilute with water and neutralise the excess of acid with sodium carbonate.

[4] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 422. 106, 1910. If the mass darkens, platinum, derived from the crucible during the bisulphate fusion, is separating.

[5] See also J. A. Phillips, *Phil. Mag.* (4), 41. 87, 1871.

as indicated on page 184, and added to the total silica of page 169. The residue in the crucible may be treated for barium, as indicated below; or fused with a little more pyrosulphate, and the cold mass, when dissolved in water, added to the main solution,[1] which is made up to 250 or 300 c.c. in a measuring flask.

Correction for Barium.—If traces of barium be retained by the silica and the alumina precipitates, it will be found in the residue in the crucible left after determining the "extra silica." It can be recovered by floating off the barium sulphate from any platinum by means of water. Fuse with potassium pyrosulphate, dissolve the cold cake in dilute sulphuric acid, collect the barium sulphate on a 5-cm. filter paper, ignite, and weigh (page 618).[2]

Correction for Platinum from the Crucible.—In exact analyses provision for the removal of platinum should always be made after a pyrosulphate or a bisulphate fusion. Platinum is readily precipitated from hot sulphate solutions by hydrogen sulphide. Some platinum may be found in the filtrate from the silica, but it is not usually necessary to remove it at this stage of the work. Hence all the platinum is not necessarily derived from the crucible during the pyrosulphate fusion, and, in consequence, if the platinum be weighed in the same crucible as that in which the bisulphate fusion was made, any excess over that lost by the crucible should be deducted from the alumina.

Errors.—The same clay, mentioned at the end of the chapter on the silica determination, was treated for the alumina, etc. The following numbers were obtained with eight independent determinations for the "ammonia" precipitate:—

0·2460; 0·2452; 0·2474; 0·2458; 0·2447; 0·2461; 0·2465; 0·2457,

with a mean value of 24·60 per cent., and a deviation of approximately ± 0·13.

The chief sources of error are: (1) Imperfect precipitation of the alumina and iron; (2) Imperfect washing of the precipitate; (3) Precipitation of lime owing to the use of "old" ammonia; (4) Imperfect dehydration; (5) Variable state of oxidation of the iron on ignition; (6) Contamination with silica subsequently dissolved in the bisulphate fusion. The imperfect washing is a most serious error, and it is probably here that beginners usually go wrong. The alumina determination is the *pons asinorum* of clay and silicate analysis.

The iron (page 187), manganese (page 372), phosphoric oxide (page 595), and titanium (page 203) are now determined in aliquot portions of the acid solution of the pyrosulphate fusion. The corrections for vanadium, rare earths, beryllium, uranium, chromium, etc., are discussed in the chapters dealing with these elements.

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[1] According to W. F. Hillebrand (*Journ. Amer. Chem. Soc.*, **24**. 369, 1902; *Chem. News*, **86**. 90, 1902), from one to two milligrams of silica still remain in solution and escape recovery.

[2] If an appreciable amount be present, it is well to prove that it really is barium sulphate by fusion with sodium carbonate, etc. If phosphoric acid be present, some titanium phosphate may be precipitated, and this may be mistaken for barium sulphate.

CHAPTER XIV.

THE DETERMINATION OF IRON.

§ 88. The Determination of Iron.

THERE is a wide choice of methods for the determination of iron depending upon volumetric, colorimetric, or gravimetric processes. In volumetric processes the ferric iron may be reduced to the ferrous condition by stannous chloride, metallic zinc, hydrogen sulphide, etc. The special features of the different processes of reduction here recommended are indicated in the text. The ferrous salt is re-oxidised to the ferric condition by a standard solution of potassium permanganate or potassium dichromate. The iron can also be determined volumetrically while in the ferric condition by titration with titanous chloride,[1] which reduces the ferric to the ferrous condition during the titration. Störmer[2] has compared permanganate and dichromate titrations with Rothe's ether process, and pronounces in favour of the permanganate titration. The permanganate process has long been a favourite on account of its simplicity, accuracy, and elegance, and it is the best process to use when the conditions are favourable; but unfortunately, as we shall soon see, it is not always satisfactory in clay analyses. The colorimetric process (page 200) has the advantage that the iron is directly determined in the ferric condition, without reduction, and it is quite satisfactory, both in speed and accuracy, for general work on clays containing less than about 2 per cent. of ferric oxide. For gravimetric processes, see pages 455 *et seq.*

§ 89. The Reduction of the Ferric to Ferrous Salts for the Permanganate Titration.

Reduction by Metallic Zinc or Magnesium.—Zinc, in spite of many objections, is the favourite method of reduction. The filtrate from the bisulphate fusion is treated with iron-free zinc[3] and dilute sulphuric acid until a drop removed on a glass rod gives no reddish-brown coloration with a drop of ammonium thiocyanate. This method is convenient and extensively employed when the titanium is ignored.

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[1] E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 11, 1910; E. Knecht and E. Hibbert, *Ber.*, **36**. 1549, 1903; E. Knecht, *ib.*, **36**. 166, 1903. A. Purgotti titrates ferric solutions with an acid solution of molybdenum oxide—Mo_3O_8 (*Gaz. Chim. Ital.*, **26**. ii. 197, 1896).

[2] M. Störmer, *Tonind. Ztg.*, **32**. 1609, 1908; R. Davidson, *Journ. Soc. Chem. Ind.*, **6**. 421, 1887; P. Lehnkering, *Zeit. öffent. Chem.*, **4**. 459, 1898.

[3] It is not easy to get zinc free from iron and carbon. G. F. Rodwell (*Chem. News*, **3**. 4, 1861) found that zinc contained about 1·3 per cent. of a black insoluble residue consisting of about 0·5 per cent. of carbon along with some lead and iron. Carbon, if present, decolorises a certain amount of permanganate, and gives high results (J. B. Mackintosh, *Chem. News*, **50**. 75, 1884). It is generally advisable to make a blank test with, say, 10 grms. of the zinc, and thus find a correction for the zinc used in the reduction. If the zinc be pure, it dissolves very slowly in acids, and even when the pure zinc is in contact with platinum a reduction may occupy 24 hours. L. Moyaux (*Rev. Univ. Mines* (1), **25**. 148, 1869) recommends amalgamated zinc. Amalgamated zinc in contact with platinum is better, but the action may stop owing

The solution under investigation is placed in an Erlenmeyer's flask. The solution should not contain more than about 0·1 grm. of Fe_2O_3 per 100 c.c.[1] Add some thin flakes of granulated zinc, or, better still, two or three portions of stick magnesium.[2] Add sufficient sulphuric acid to make a solution containing about 17 per cent. of H_2SO_4.[3] The flask is closed with a one-hole rubber stopper fitted with a Bunsen's valve (fig. 101) or a Binder's (fig. 102),[4] or, better, with a

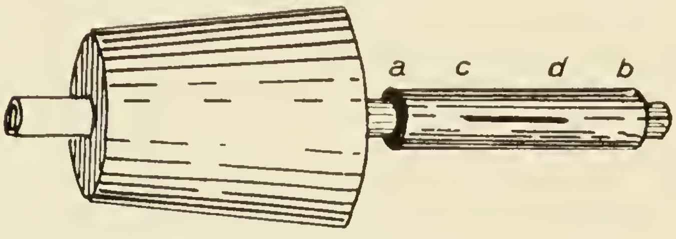

FIG. 101.—Bunsen's valve.

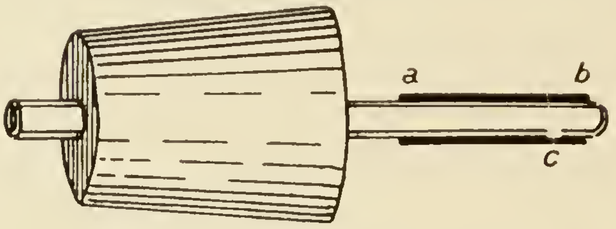

FIG. 102.—Binder's valve.

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to the amalgamation of the platinum during the action (A. L. Beebe, *Chem. News*, **53**. 269, 1886). To amalgamate zinc, shake it in a flask with a solution of mercuric sulphate in 2·5 per cent. sulphuric acid (1 grm. metallic mercury per 100 grms. of zinc). Wash the metal several times with 2·5 per cent. sulphuric acid, and finally with water. G. T. Morgan (*Analyst*, **26**. 225, 1901 ; J. H. Gladstone, *Chem. News*, **32**. 75, 195, 1875 ; J. H. Gladstone and A. Tribe, *ib.*, **32**. 150, 1875) recommends a zinc-copper couple in a 3 per cent. solution of sulphuric acid. The zinc-copper couple is made by immersing, say, 8 grms. of granulated zinc in 200 c.c. of a 10 per cent. solution of copper sulphate. The action is said to be much more rapid than with zinc alone. For the aluminium reduction in hot solutions, see F. J. R. Carulla, *Journ. Soc. Chem. Ind.*, **27**. 1049, 1908 ; W. H. Seamon, *Chem. Eng.*, **8**. 124, 1908. Aluminium foil does its work more rapidly than zinc, but it too must be corrected for iron. Magnesium ribbon is generally free from iron, phosphorus, and sulphur. It reduces much more rapidly than zinc (S. Kern, *Chem. News*, **33**. 112, 1876 ; H. N. Warren, *ib.*, **60**. 187, 1889), but is liable to float on the surface of the solution. This latter objection does not apply to sticks of metallic magnesium, which is in many ways preferable to zinc—but the cost is a little greater. A. Gemmell (*Analyst*, **35**. 65, 1910) recommends zinc-aluminium and magnesium-zinc (magnalium) alloys for some reductions. For reductions with palladium-hydrogen, see L. Kritschewsky, *Ueber die Anwendung des metallischen Wasserstoffs in der analytischen Chemie*, Bern, 1885 ; W. H. Gintl, *Zeit. angew. Chem.*, **15**. 424, 1902 ; A. C. Chapman, *Analyst*, **29**. 346, 1904. For the efficiency of different reducing agents, see A. C. Chapman and H. D. Law, *ib.*, **31**. 3, 1906. For reduction with metallic copper, see L. Storch, *Ber. Oester. Ges. Förder. Chem. Ind.*, **15**. 9, 1893 ; W. C. Birch, *Chem. News*, **99**. 273, 1909.

[1] A. Mitscherlich (*Zeit. anal. Chem.*, **2**. 72, 1863) says that there is a danger of loss owing to the precipitation of some metallic iron on the zinc—N. W. Fischer, *Pogg. Ann.*, **9**. 266, 1827. The iron dissolves when the last trace of zinc dissolves. There is, however, no danger under this head when the solutions are diluted and acidified as indicated in the text. E. Müller and G. Wegelin (*Zeit. anal. Chem.*, **50**. 615, 1911) note the danger indicated by Mitscherlich, and recommend reducing the ferric iron by adding 5–10 drops of $N\text{-}CuSO_4$ and warming the solution with amalgamated zinc rods for a couple of hours.

[2] 10 grms. of metallic zinc, or 4 grms. of metallic magnesium, usually suffice for reducing 0·1 grm. of ferric oxide.

[3] That is, about 20 c.c. of concentrated sulphuric acid per 100 c.c. of the solution (sp. gr. 1·8). Note the amount of acid already present in the solution.

[4] For a Bunsen's valve (fig. 101), fit the hole in the stopper with a piece of short glass tubing (*a*, fig. 101), to which is attached a piece of indiarubber tubing plugged at the other end with a piece of glass rod (*b*). The rubber tubing has a longitudinal slit (*cd*). It readily permits the outflow of gas, but offers some opposition to the back flow of air. The valve will sometimes hold so well that the flask will break before the valve gives way, particularly when the contents of the flask have been heated and allowed to cool with the Bunsen's valve in position. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 278, 1853 ; A. Krönig, *Pogg. Ann.*, **122**. 170, 1864 ; C. H. Bostock, *Chem. News*, **57**. 213, 1890 ; U. Kreusler, *Zeit. anal. Chem.*, **24**. 393, 1885 ; O. Binder, *ib.*, **27**. 178, 1888 ; O. Reitmar and A. Stützer, *Rep. anal. Chem.*, **5**. 232, 1885 ; L. R. Milford, *Journ. Ind. Eng. Chem.*, **4**. 845, 1912. The construction of Binder's valve will be obvious from fig. 102, where *c* represents a small aperture in the side of a glass tube closed at one end ; and *ab*, a piece of rubber tubing.

Kempf's or a Schiebler's gas-washer as guard tube.[1] These vessels are glass bulbs fitted inside with a syphon tube as shown in fig. 103. Water is poured into the bulb until the free end of the inner tube just dips below the surface. When the iron is reduced, pour an aqueous solution of sodium bicarbonate into the bulb. As the flask cools, the carbonate solution is drawn into the flask, and carbon dioxide is given off. When equilibrium is established, the contents of the flask are well protected from the air by the carbon dioxide. The flask may be warmed to facilitate the reduction. The reduction is complete when a drop of the solution gives no red coloration with a drop of ammonium thiocyanate.[2] The flask may be heated until all the zinc is dissolved; or the undissolved zinc and carbon may be filtered off through glass-wool. There is a great risk of re-oxidation during the filtration.[3] If the titanium is to be neglected, the solution can be titrated at once with standard permanganate as described below.

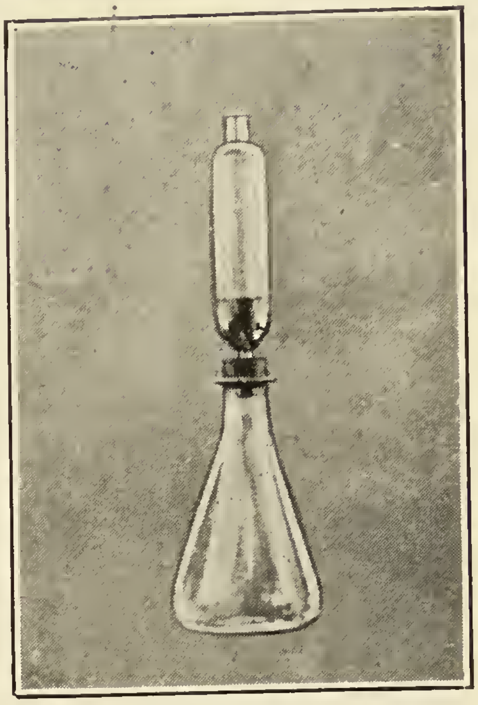

FIG. 103.—Reduction in flask fitted with guard tube.

Effect of Titanium.—When titanium is present,[4] the zinc reduces, more or less completely,[5] the titanic oxide to titanium sesquioxide: $2TiO_2 \rightarrow Ti_2O_3$, etc. The latter is re-oxidised to titanic oxide, TiO_2, during the permanganate titration.[6] In consequence, more or less[7] titanium is estimated as if it were iron. It is by no means uncommon to find clays with $\frac{1}{2}$ to 4 per cent. of titanic oxide, and such clays would be reported with $\frac{1}{2}$ to 4 per cent. of ferric oxide more than that actually present. This is a serious matter.[8] If, therefore, the zinc reduction be adopted, the titanium should be re-oxidised by adding a little bismuth oxide to the reduced solution. According to Gooch and Newton,[9] this treatment will oxidise the Ti_2O_3 without affecting the ferrous salt. The reduced solution should be filtered in order to remove the unreduced bismuth oxide and bismuth. In illustration of the effect of bismuth oxide, Gooch and Newton quote the following test experiments:—

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[1] T. Kempf, *Zeit. anal. Chem.*, 7. 442, 1868; W. T. K. Stock, *Chem. News*, 39. 46, 1879; R. Jahoda, *Zeit. angew. Chem.*, 12. 87, 1890; H. Göckel, *ib.*, 12. 620, 1899; *Chem. Ztg.*, 37. 235, 1913; A. Contat, *ib.*, 22. 298, 1895; M. Spang, *ib.*, 36. 1465, 1912; M. Mittenzwey, *Journ. prakt. Chem.* (1), 91. 86, 1864. Several other devices have been used.

[2] This test will indicate one part of iron in 1,600,000 parts of water—A. Wagner, *Zeit. anal. Chem.*, 20. 349, 1881; E. F. Smith (*ib.*, 19. 350, 1880) says 1 in 80,000,000. A. Ebeling (*Zeit. öffent. Chem.*, 8. 144, 1901) adds the potassium thiocyanate to the solution being reduced; J. Volhard (*Zeit. angew. Chem.*, 14. 609, 1901) says Ebeling's method is not trustworthy, because (1) nascent hydrogen reduces the KCNS and leads to low results; (2) any excess of KCNS leads to an increased consumption of the permanganate.

[3] According to M. M. P. Muir (*Chem. News*, 97. 50, 1908), the addition of 100 c.c. of a saturated solution of mercuric sulphate stops the reaction. MERCURIC SULPHATE SOLUTION.—Mix 20 grms. of mercuric sulphate with 8 c.c. of concentrated sulphuric acid, and stir up the pasty mass with 80 c.c. of water. If a yellow precipitate separates, add more sulphuric acid. Note the danger suggested by Mitscherlich, page 188.

[4] The solution reduces more quickly apparently owing to the catalytic action of titanic oxide.

[5] See page 199.

[6] F. O. von der Pfordten, *Liebig's Ann.*, 234. 257, 1886; 237. 201, 1887; F. Pisani, *Compt. Rend.*, 59. 289, 1864; A. Gemmel, *Analyst*, 35. 198, 1910; C. Marignac, *Zeit. anal. Chem.*, 7. 112, 1868; E. Wiegand, *ib.*, 21. 510, 1882; H. A. Wells and W. L. Mitchell, *Journ. Amer. Chem. Soc.*, 17. 78, 1895; G. Gallo, *Atti Accad. Lincei* (5), 16. i. 525, 1907; H. D. Newton, *Amer. J. Science* (4), 25. 130, 1907; *Chem. News*, 98. 134, 1908; F. W. Hinrichsen, *Chem. Ztg.*, 31. 738, 1907; E. Knecht and E. Hibbert, *Analyst*, 36. 96, 1911.

[7] "More or less" because, while acid solutions of ferrous sulphate oxidise slowly on exposure to air, titanous sulphate oxidises very quickly, and this oxidation is the principal difficulty in the volumetric determination of titanium by this reaction.

[8] For the effect of vanadium, see pages 467 and 480.

[9] F. A. Gooch and H. D. Newton, *Amer. J. Science* (4), 23. 365, 1907; *Zeit. anorg. Chem.*, 54. 213, 1907; *Chem. News*, 96. 148, 1907; H. D. Newton, *ib.*, 98. 218, 1908; *Amer. J.*

Table XXXIV.—Effect of Bismuth Oxide in inhibiting the Effect of Titanium in the Permanganate Process for Iron.

Grm. TiO_2 taken.	Grm. Fe_2O_3 taken.	Grm. Fe_2O_3 found.	Error.
0·04	0·0993	0·0992	− 0·0001
0·06	0·0993	0·0993	0·0000
0·08	0·0993	0·0997	+ 0·0004
0·1	0·0993	0·0997	+ 0·0004
0·2	0·0993	0·0997	+ 0·0004
0·1	0·1986	0·1986	0·0000

It is difficult to filter a ferrous solution without re-oxidation of a portion of the ferrous salt. A filtration flask can be fitted with a filter tube packed with a layer of broken glass beneath a layer of calcined quartz sand. A couple of fragments of magnesite (iron-free) are placed in the filtration flask along with about 2 c.c. of dilute sulphuric acid; another couple of fragments of magnesite are placed in the filter tube, and in the flask containing the reduced solution. The filter flask is connected with the pump, and the solution under investigation is poured into the filter tube. The flask is washed with dilute sulphuric acid with a couple of fragments of magnesite placed in the flask at each washing. In this way, an atmosphere of carbon dioxide may be kept between the solution containing the reduced iron and the atmosphere.[1] The solution in the filtration flask may then be titrated with permanganate without interference from the titanium.

The Reductor.—The apparatus suggested by Jones[2] can be employed for rapid zinc reductions. A modification is illustrated in fig. 104. A piece of glass tubing—40 to 45 cm. long and 12 to 15 mm. internal diameter—is drawn out at one end, and there fitted into the neck of a filtration flask by means of a one-hole rubber stopper. The other end of the tube is fitted with a stoppered funnel, or rubber tube and pinchcock. Put a filter plate or a few pieces of broken glass into the lower portion of the tube, then about 2½ cm. of coarse, clean, calcined quartz sand. Fill the tube with about 200 to 300 grms. of amalgamated or ordinary zinc powder[3] granulated to pass a 20's lawn, and remain on a 30's lawn. The zinc should be as free from iron as possible.[4] To

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Science (4), **25**. 343, 1908; R. Rieke and R. Betzel, *Sprech. Archiv*, **1**. 45, 1912. For copper sulphate and copper oxide instead of bismuth oxide, see W. C. Birch, *Chem. News*, **99**. 272, 1909; A. Storch, *Ber. Oester. Ges. Förder. Chem. Ind.*, **15**. 9, 1893.

[1] For more elaborate schemes, see W. Bachmeyer, *Zeit. anal. Chem.*, **24**. 59, 1885; N. von Klobukow, *ib.*, **24**. 395, 1885.

[2] D. J. Carnegie, *Journ. Chem. Soc.*, **53**. 468, 1889; C. Jones, *Trans. Amer. Inst. Min. Eng.*, **17**. 414, 1889; *Chem. News*, **60**. 93, 1889; P. W. Shimer, *Journ. Amer. Chem. Soc.*, **21**. 723, 1899; E. H. Miller and H. Frank, *ib.*, **25**. 919, 1903; D. L. Randall, *ib.*, **28**. 389, 1900; *Amer. J. Science* (4), **24**. 313, 1907; *Chem. News*, **97**. 113, 1908; C. B. Dudley and F. N. Pease, *Journ. Anal. App. Chem.*, **7**. 108, 1893; F. L. Crobough, *ib.*, **6**. 366, 1892.

[3] The use of amalgamated zinc (proposed by A. J. McKenna) in place of ordinary zinc, enables a shorter reductor to be used. This is due to the more vigorous action of the amalgamated zinc.

[4] Commercial zinc dust is generally less pure than the granulated metal. It contains cadmium, lead, and zinc oxide, together with iron, etc. Zinc, at 210°, is very brittle, and it

use the apparatus, close the stopcock; pour 100 c.c. of cold dilute sulphuric acid (1 : 20)[1] into the funnel. Apply suction at the filtration flask, since the hydrogen evolved retards the percolation of the acid through the tube. Open the stopcock to allow the acid to pass slowly through the column of granulated zinc. Wash the zinc free from acid with about five rinsings of distilled water. Repeat the treatment with acid and water. Close the stopcock so that the tube remains full of water. Disconnect the filtration flask, wash and restore it to its place. The tube is now ready for use.

Pour the iron solution[2] to be reduced into the funnel. Connect the filtration flask with the pump. Open the stopcock cautiously, since the rate of flow of the solution to be reduced is regulated by the stopcock. As the solution flows through the column of zinc, complete reduction occurs, and the solution collects in the filtration flask ready for titration or for treatment with bismuth oxide. Just before the funnel is emptied, spirt water round the sides, and also rinse the beaker with water. Let the washings collect in the funnel, and ultimately pass them through the column of zinc.[3] Wash the column of zinc with distilled water as before. The reductor is then ready for another reduction.

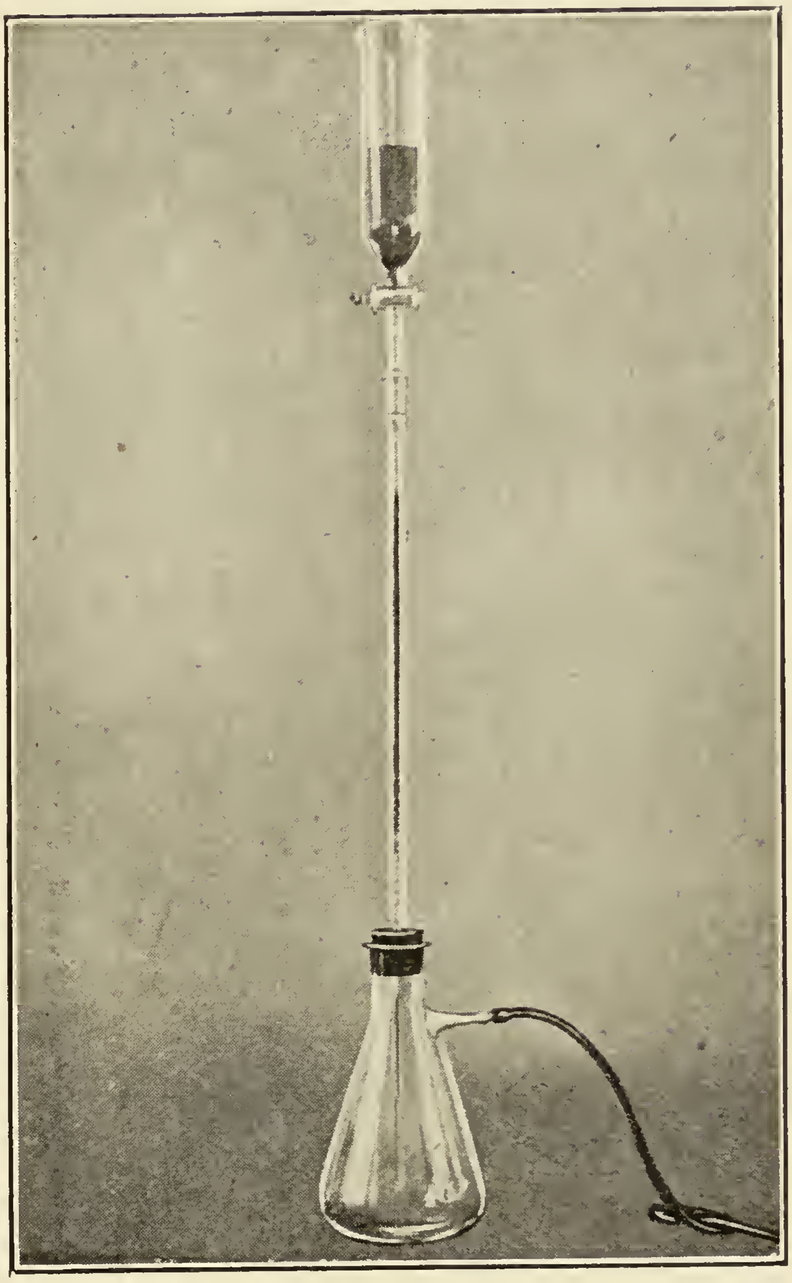

Fig. 104.—Reductor.

The reductor should be tested from time to time with blank tests. A correction for the iron in the zinc can be made by re-reducing the solution used in the permanganate titration. The amalgamated zinc in the tube charged as indicated above will suffice for thirty to forty reductions.

Reduction by Ammonium Bisulphite.—Hydrogen sulphide, sulphur dioxide,

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can be easily reduced to fine grains by trituration at this temperature—T. M. Brown, *Iron*, **12.** 361, 1878; *Dingler's Journ.*, **228.** 378, 1879.

[1] The ratio of free sulphuric acid (sp. gr. 1·84) to the total solution should be between 1 : 5 and 1 : 6. If more acid be present than 1 : 5, zinc sulphate is inclined to crystallise in the reductor; and if less than 1 : 7 be present, the reduction may not be complete in the case of uranium solutions—E. F. Kern, *Journ. Amer. Chem. Soc.*, **23.** 685, 1901; F. Ibbotson and S. G. Clark, *Chem. News*, **103.** 146, 1911. A. A. Blair (*The Chemical Analysis of Iron*, Philadelphia, 92, 1908) used the reductor for phosphorus determination; F. A. Gooch and G. Edgar (*Chem. News*, **87.** 265, 1903; *Amer. J. Science* (4), **25.** 233, 1908) for vanadium; G. Edgar (*ib.* (4), **25.** 332, 1908) for vanadium and molybdenum; and by E. F. Kern (*Journ. Amer. Chem. Soc.*, **23.** 685, 1901; F. Ibbotson and S. G. Clark, *Chem. News*, **103.** 146, 1911) for uranium; see phosphorus, page 599.

[2] The iron solution should not contain more than about 15 c.c. of concentrated sulphuric acid per 100 c.c. of solution.

[3] In washing the reductor free from iron the water should be kept above the level of the zinc, so as not to allow any air spaces between the successive additions of water. There is otherwise a possible formation of hydrogen peroxide which might spoil the results.

ammonium bisulphite, or sodium sulphite can be used for reducing the iron. These agents have the advantage of leaving the titanic oxide unaffected. Ammonium bisulphite, recommended by Austin and Hurff,[1] is convenient. It can be either made or purchased.[2] The solution under investigation is concentrated by evaporation to 40 or 50 c.c. Gradually add about 10 c.c. of dilute sulphuric acid (1:1) to the solution in an Erlenmeyer's flask, so as to make the solution distinctly acid.[3] Add a concentrated solution of ammonium bisulphite;[4] and agitate the mixture thoroughly; or pass a current of sulphur dioxide through the acid solution. Gradually raise the temperature of the solution to boiling, and when a drop no longer gives a brownish-red coloration with ammonium thiocyanate, the ferric oxide is all reduced.

To remove the excess of sulphurous acid, place the flask on a sheet of asbestos on a tripod. Add 15 c.c. of dilute sulphuric acid (1 : 1). Cover the flask with the perforated lid of a Rose's crucible.[5] Pass a current of carbon dioxide at the rate of 3 or 4 bubbles per second through the solution.[6] The delivery tube passes through the hole in the cover of the flask. Meanwhile the flask is heated to the boiling point of the solution. The velocity of the carbon dioxide is then reduced to about 1 bubble per second. After 20 or 30 minutes' boiling, the escaping steam will probably be free from sulphur dioxide, as shown by its failure to discolour a mercurous nitrate test paper.[7] In that case, place the flask in a dish of cold water to cool, while the current of carbon dioxide still bubbles through the solution—1 bubble per second.[8]

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[1] P. T. Austen and G. B. Hurff, *Chem. News*, **46**. 287, 1882; *Amer. Chem. Journ.*, **4**. 282, 1882; T. W. Hogg, *Chem. News*, **59**. 207, 1889; R. W. Atkinson, *ib.*, **49**. 217, 1884. According to B. Glasmann (*Zeit. anal. Chem.*, **43**. 506, 1904), the ammonium sulphite does not reduce bichromic sulphate and hence the presence of chromium does not interfere.

[2] AMMONIUM BISULPHITE.—Pass sulphur dioxide into a concentrated solution of ammonia until the solution becomes yellow and smells strongly of sulphur dioxide. If the solution be kept cool during the passage of the gas, white crystals of neutral sulphite are formed. These are gradually dissolved by the excess of sulphur dioxide, and the solution becomes clear yellow. For the sulphur dioxide, use either a syphon of the liquid gas, or boil copper with concentrated sulphuric acid in the proportion 250 grms. of copper and 500 c.c. of concentrated sulphuric acid. 18 c.c. of this solution will reduce about 10 grms. of ferric oxide. G. Neumann (*Ber.*, **20**. 1584, 1881) makes sulphur dioxide in a Kipp's apparatus by the action of concentrated sulphuric acid on cubes made from three parts calcium sulphite and one part plaster of Paris. This method is not suited for very large quantities of the gas. Sulphur dioxide is best purchased in "syphons" of the liquefied gas. The "syphons" are a convenient source of the gas for analytical work.

[3] The reduction of ferric solutions by sulphur dioxide proceeds rapidly if the solution contains a little free acid, but not if the solution is alkaline to litmus—A. C. Cumming and E. W. Hamilton, *Proc. Roy. Soc. Edin.*, **32**. 12, 1912.

[4] 1 c.c. of the solution per 0·5 grm. of Fe_2O_3.

[5] Or bend down the corners of a piece of platinum foil with two holes: one hole permits the escape of steam and gas; the other is for the gas delivery tube.

[6] The carbon dioxide is washed by passing it through a column of pumice soaked in copper sulphate and a water wash-bottle.

[7] MERCUROUS NITRATE TEST PAPER.—A piece of mercurous nitrate test paper held in the vapour becomes brownish black if sulphur dioxide be in the escaping steam. The paper is made by soaking No. 00 Swedish filter paper in a solution of mercurous nitrate (0·5 to 5 per cent.) and drying. The paper is cut in strips and preserved for use in dry glass tubes, corked and sealed. H. Jervis (*Chem. News*, **77**. 133, 1898) closes the flask with a stopper fitted with a syphon-like tube, one end of which is dipped into an acid, very dilute solution of permanganate. If the solution be completely decolorised (without a brown precipitate), sulphur dioxide is still being evolved.

[8] As a matter of fact, it is rather difficult to remove the last trace of sulphur dioxide, and if all be not removed the iron determination will be high. The condensation of water in the neck of the flask and on the stopper is the main source of the trouble, for the condensed water absorbs some sulphur dioxide and, on dropping back into the solution, returns some sulphur dioxide. For the retention of sulphur dioxide by rubber stoppers and rubber tubing, see E. W. Hamburger, *Zeit. physiol. Chem.*, **2**. 191, 1878; **4**. 249, 1880; K. H. Huppert, *ib.*, **17**. 87, 1893.

When cold, the contents of the flask can be titrated with a standard solution of potassium permanganate, as indicated below. The titanium oxide is not reduced by the treatment with ammonium bisulphite.

§ 90. The Standardisation and Use of Potassium Permanganate Solution.

The "commercially pure" potassium permanganate picks up dust, etc., and is rather poorer in oxygen than theory requires,[1] although, by repeated crystallisation from boiling water and careful drying the salt can be prepared to give a solution of exactly theoretical strength.[2] It is, however, the invariable custom to find the strength, that is, to standardise the solution of potassium permanganate.

Standard Solution of Sodium Oxalate.—Dissolve about a gram of potassium permanganate ($KMnO_4$, molecular weight 158·03) in a litre of water, and let the solution stand two or three weeks in order that the permanganate may oxidise any impurities in the water before the solution is standardised by titration with, say, a solution of sodium oxalate of known strength. Other salts are in common use, but sodium oxalate gives exact results with very little trouble. Whatever salt be selected, the standard solution must be made up with the greatest care, since all the subsequent results depend upon the accuracy of the work at this stage. Sörensen's sodium oxalate[3] ($Na_2C_2O_4$, molecular weight 134) is the best "brand" for the purpose. This salt is dried in a water oven at about 200° and cooled in a desiccator over calcium chloride. Transfer 2·13 grms. of the salt to the litre flask. Dissolve the salt in a little water, make the solution up to a litre mark. One cubic centimetre will be equivalent to 0·001 grm. of $KMnO_4$, or to 0·00253 grm. Fe_2O_3. This solution can be used for standardising the permanganate. The equivalents of other substances can easily be expressed in terms of sodium oxalate by means of the usual chemical equation (page 194).

The following table of conversions may be useful for reference :—

Table XXXV.—Conversion Table for Permanganate Solutions.

One gram of	is equivalent to							
	Fe.	FeO.	$K_2Cr_2O_7$.	Fe_2O_3.	$Na_2C_2O_4$.	$KMnO_4$.	$FeSO_4$ $(NH_4)_2$ SO_4 $6H_2O$.	CaO.
Iron . .	1·0000	1·28613	0·8782	1·42919	1·1992	0·56555	7·01514	0·50198
Sodium oxalate	0·8336	1·0724	0·7324	1·1918	1·0000	0·4716	5·8369	0·4186
Potassium permanganate	1·76819	2·27412	1·5528	2 52708	2·1204	1·0000	12·404	0·8876
Ferrous ammonium sulphate	0·14255	0·18334	0·1249	0·20373	0·17055	0·08062	1·0000	0·07139
Potassium bichromate	1·1383	1·4644	1·0000	1·6274	1·3655	0 64388	8·0064	0·5716

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[1] According to F. Raschig (*Zeit. angew. Chem.*, **16.** 585, 1904), a solution prepared from commercial permanganate was about 0·8 per cent. too weak.

[2] W. M. Gardner, B. North, and A. R. Naylor, *Journ. Soc. Chem. Ind.*, **22.** 731, 1903.

[3] S. P. L. Sörensen, *Zeit. anal. Chem.*, **36.** 639, 1897 ; **42.** 333, 512, 1903 ; **44.** 141, 1905 ; S. P. L. Sörensen and A. C. Andersen, *ib.*, **44.** 156, 1905 ; L. Vanino and E. Seitter, *ib.*, **41.**

Standardisation of Potassium Permanganate with Sodium Oxalate.—Pipette 25 c.c. of the standard sodium oxalate solution into each of three Erlenmeyer's flasks; add 10 c.c. of dilute sulphuric acid (1 : 4). Place the flask under a glass-stoppered burette filled with the permanganate solution to be standardised, and warm the oxalate solution to between 60° and 70°. Run permanganate from the burette into the flask, and keep the contents of the flask in a state of rotary agitation while the permanganate is being added. The colour of the permanganate is discharged slowly at first. It is an advantage to work with the solution at about 60° or 70° in order to accelerate the action. When the reaction first starts, it proceeds very slowly; afterwards it progresses more rapidly. When the colour of the permanganate begins to disappear slowly, add the permanganate very cautiously, drop by drop. Any drops of permanganate adhering to the sides of the flask must be washed into the bulk of the liquid. When a drop of the permanganate produces a permanent pink blush throughout the liquid in the flask, the titration is finished. Read the burette to the nearest tenth. Take the mean of three such titrations.

Let n denote the number of cubic centimetres of the permanganate solution required for the titration of the 25 c.c. of sodium oxalate solution. The reaction is symbolised:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 5Na_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Since 1000 c.c. of the sodium oxalate solution are equivalent to 1 grm. of $KMnO_4$, 25 c.c. will be equivalent to 0·025 grm. of $KMnO_4$. Hence, n c.c. of the permanganate solution has the equivalent of 0·025 grm. $KMnO_4$, and this is equivalent to 0·06317 grm. of Fe_2O_3. Or, 1 c.c. of the permanganate solution is equivalent to $0·0632 \div n$ grm. Fe_2O_3. The error with careful work is about one part in a thousand.

Influence of Acids.—Sulphuric acid is required to decompose the oxalate, and in titrating with permanganate, free acid is needed to keep the manganese oxides in solution. Otherwise, the brown precipitate which separates will obscure the end point. Too much sulphuric acid may lead to high results, since concentrated sulphuric acid reduces potassium permanganate. This is illustrated by the following experiments,[1] with 20 c.c. of an acidified solution of ferrous sulphate containing the equivalent of 0·080 grm. Fe_2O_3, and with various proportions of sulphuric acid (1 : 4). The volume of the permanganate solution required with different quantities of the acid is indicated by the following numbers:

H_2SO_4 . . .	0	10	20	25	40	50	c.c.
$KMnO_4$ . . .	17·89	17·85	17·89	18·07	18·20	18·62	c.c.

To show that the increased consumption of permanganate was not due to impurities in the sulphuric acid, 150 c.c. of water and 50 c.c. of the same sulphuric acid were added to another 50 c.c. of the ferrous solution. The consumption of permanganate was practically the same as when a solution of the ferrous salt diluted with water only was employed.

Hydrochloric acid is baneful because some permanganate is used in the side reaction, possibly:

$$16HCl + 2KMnO_4 = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O,$$

141, 1902; A. Skrabal, *ib.*, **42**. 359, 1903; C. Meineke, *ib.*, **39**. 322, 1900; G. Lunge, *Zeit. angew. Chem.*, **17**. 230, 269, 1904; **18**. 1520, 1905; F. Dupré and E. Müller, *ib.*, **15**. 1244, 1902; F. Dupré, *ib.*, **17**. 815, 1904; F. Dupré and A. von Küpffer, *ib.*, **15**. 352, 1902; W. Schranz, *Bull. Soc. Chim.* (3), **18**. 89, 1899; H. Kinder, *Chem. Ztg.*, **30**. 631, 814, 1906; **31**. 69, 1907; P. Lehnkering, *ib.*, **30**. 723, 1906; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **44**. 14, 1896; S. M'Bride, *Journ. Amer. Chem. Soc.*, **34**. 393, 1912; *Circ. Bur. Standards*, **40**. 3, 1912.

[1] E. Waitz, *Zeit. anal. Chem.*, **10**. 158, 1870; J. P. Blunt, *Chem. News*, **8**. 54, 1863.

which proceeds slowly in dilute solutions, but is accelerated by the presence of iron salts. Similar experiments to those indicated in the last paragraph were made with hydrochloric acid (sp. gr. 1·13). The results were:

HCl . . .	0	5	10	15	20	30	c.c.
$KMnO_4$ . . .	17·89	19·25	19·75	20·12	20·50	20·50	c.c.

The side reaction is inhibited by the addition of manganese sulphate, as indicated on page 451.

Nitric acid should be absent, because it is reduced to nitrous acid by the zinc in the reduction of the ferric oxide, and nitrous acid reduces the permanganate.[1]

Standardisation of Potassium Permanganate with Metallic Iron.—It is nearly always advisable, if convenient, to standardise a volumetric solution against a solution similar to that which is going to be titrated. Hence, many prefer to standardise the permanganate solution for iron determinations against a solution containing a known amount of metallic iron dissolved in, say, sulphuric acid. The difficulty is with the iron. Perfectly pure iron is exceedingly difficult to procure. The trace of impurity present in most specimens of "pure" iron acts as a reducing agent on the permanganate. Even electrolytic "iron" is not quite free from objection.[2] It is frequently assumed that iron wire contains on an average 0·3 per cent. of foreign impurities—the variations lie usually between 0·1 and 0·4 per cent. The amount of iron actually weighed out is accordingly multiplied by 0·997 in order to estimate the strength of the solution. It is then supposed that the impurities in the iron wire diminish the amount of metal acted upon by the permanganate and exert no other reducing action. This assumption is not justified. The impurities, carbon, sulphur, etc., are present as carbides, sulphides, phosphides, silicides, etc., and these substances develop hydrocarbons, hydrogen sulphide, hydrogen phosphide, etc., when the iron wire is dissolved in sulphuric acid. These products are easily oxidised by permanganate. The consequence is that more permanganate is used than corresponds with the amount of iron in the wire, and the permanganate titre is accordingly too low. An error ranging from 1 to 2 per cent. may be committed in standardising potassium permanganate by means of iron wire assumed to represent pure iron, and the error is increased instead of diminished by assuming that the wire contains less than its own weight of iron.[3]

Samples of "analysed" iron can be purchased, but these are not satisfactory for standardising the permanganate unless their iron value has been determined in terms of the permanganate. This is a troublesome determination in a technical laboratory.[4] Satisfactory samples with a known permanganate titre can be purchased.[1] The iron wire is cleaned, if necessary, with sandpaper to remove grease or oil, and dissolved in sulphuric acid at a gentle heat in a 200-c.c. flask fitted like fig. 103, and from which the air has been previously expelled by a stream of carbon dioxide. The cold solution is titrated with permanganate, as previously described.

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[1] A. Terreil, *Zeit. anal. Chem.*, **6**. 116, 1867.

[2] C. F. Roberts, *Amer. J. Science* (3), **48**. 290, 1894; *Chem. News*, **70**. 189, 1894; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 499, 1911; A. Classen, *Zeit. anal. Chem.*, **242**. 516, 1903; F. Mohr, *Lehrbuch der chemisch. analyt. Titriermethods*, Braunschweig, 215, 1896; A. Skrabel, *Zeit. anal. Chem.*, **42**. 395, 741, 1903; **43**. 97, 1904; G. Lunge, *Zeit. angew. Chem.*, **17**. 265, 1904; H. Theile and H. Deckert, *ib.*, **14**. 1233, 1901; A. Dupré, *ib.*, **17**. 815, 1904; S. Avery and B. Dale, *Ber.*, **32**. 64, 2233, 1899; H. Verwer and F. Groll, *ib.*, **32**. 806, 1899; H. Verwer, *Chem. Ztg.*, **25**. 792, 1901; H. Kinder, *ib.*, **31**. 69, 117, 1907; L. Brandt, *ib.*, **32**. 812, 830, 840, 851, 1908; C. A. Kohn, F. J. Brislee, and H. H. Froysell, *B. A. Rep.*, 174, 1900; L. Moyaux, *Rev. Univ. Mines* (1), **25**. 148, 1869; H. Cantoni and M. Basadonna, *Ann. Chim. Anal.*, **9**. 365, 1904; A. Ledebur, *Stahl Eisen*, **22**. 1242, 1902; H. Kinder, *ib.*, **30**. 411, 1910; L. Brandt, *ib.*, **30**. 1844, 1910; W. M. Gardner, B. North, and A. R. Naylor, *Journ. Soc. Chem. Ind.*, **22**. 731, 1903.

[3] J. R. M. Irby, *Chem. News*, **30**. 142, 1874; M. Berthelot, *Bull. Soc. Chim.* (2), **21**. 58, 1874.

[4] This is made by using electrolytic iron or sodium oxalate.

Higher results are obtained if the solution is made on a water bath in a flask fitted with a Bunsen's valve than if the iron be dissolved in a similar flask kept for a long time "on the boil." In the former case, the solution contains more of the impurities than in the latter case. Similarly, if the dissolution be conducted in a flask through which a current of carbon dioxide is passing, the results depend upon the duration of the boiling and the speed at which the carbon dioxide is passed. But if the carbon dioxide be passed for a long time, the results are the same whether the iron be dissolved on the water bath or at a boiling temperature.

Suppose 1 grm. of "analysed" iron wire contains the equivalent of 0·9991 grm. iron so far as the permanganate solution is concerned, this amount of iron is equivalent to $0·9991 \times 1·4292 = 1·4279$ grms. of Fe_2O_3. If w gram of the sample of iron be taken, and n c.c. of permanganate are required for the titration, obviously, 1 c.c. of the permanganate is equivalent to $1·4279\ w \div n$ grm. of ferric oxide.

However, the manipulations with Sörensen's sodium oxalate are a little easier than with metallic iron, and the results appear quite as satisfactory.[2]

Preservation of Permanganate Solutions.—Permanganate solutions should be stored in a bottle with a well-fitting glass stopper. The stopper must not be greased. The bottle must be protected from direct sunlight. Solutions containing suspended oxide are liable to lose strength, and this with increasing rapidity with the lapse of time owing to the increase in the quantity of the suspended oxide.[3] Solutions of permanganate, freed from suspended oxide by filtration through asbestos, may have a lower "titre" after filtration than before, since asbestos exerts a slight reducing action on solutions of potassium permanganate.[4] The solution will keep a long time if it be kept out of contact with organic matter, dust, etc.[5] For the best work the solution should be standardised about every two months, but after keeping through the summer months, about nine months, a solution with a titre 1 c.c. $= 0·002576$ grm. Fe_2O_3 only changed to 1 c.c. $= 0·002522$ grm. Fe_2O_3,—that is, about 2 per cent. The stock bottle should be shaken before use in order to remove any water condensed in the upper part of the bottle by distillation from below.

Burettes for the Permanganate Titration.—Glass-stoppered burettes must be employed; for regular work that shown in fig. 105 or in fig. 18 (right) is excellent. The solution of permanganate must not come in contact with organic matter from, say, rubber jets, lubricant of stopcock, etc. Scheibler[1] recommends a burette shaped like fig. 106. The flow of liquid from the burette is regulated by the stopcock or pinchcock *A*. The tube *B* is stuffed with glass- or cotton-wool to filter the air from dust before entering the burette. The burette is filled by dipping the nozzle at *C* in the fluid and applying suction at *D*. The nozzle is protected by a ground cap *C* when the burette is not in use. These burettes work well provided changes in temperature or pressure do not occur while the solution is in the burette, otherwise the solution may be forced from the jet by the expansion of the imprisoned air on a rising temperature or a diminishing pressure, and there is then an objectionable "sloppiness" about the nozzle of the burette. The advantage claimed is that

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[1] A. Müller, *Stahl Eisen*, **26**. 1477, 1906. A sample recently purchased contained: carbon, 0·027; silicon, 0·013; phosphorus, 0·034; copper, 0·024; manganese, 0·005; sulphur, 0·008—total impurities, 0·111 per cent. The "iron value" of the sample in terms of permanganate was equivalent to 99·91 per cent. metallic iron.

[2] Note that if the "permanganate titre" of the iron wire be determined by titration with sodium oxalate, the use of the iron wire appears redundant.

[3] H. N. Morse, A. J. Hopkins, and M. S. Walker, *Amer. Chem. Journ*, **18**. 401, 1896; H. N. Morse and C. L. Reesc, *ib.*, **20**. 1898; *Chem. News*, **78**. 77, 90, 1898. For the slow development of oxygen with dilute sulphuric acid solutions of potassium permanganate, see G. Blau and T. Wallis, *Liebig's Ann.*, **345**. 261, 1906; F. A. Gooch and E. W. Danner, *Ber.*, **26**. 267, 1893; W. Blum, *Journ. Amer. Chem. Soc.*, **34**. 1379, 1912.

[4] P. A. Tscheihwile, *Journ. Russ. Phys. Chem. Soc.*, **42**. 856, 1910.

[5] R. W. Oddy and J. B. Cohen, *Journ. Soc. Chem. Ind.*, **9**. 17, 1890; W. M. Gardner and B. North, *ib.* **23**. 599, 1904; B. Collitt, *Pharm. Journ.* (4), **27**. 724, 1908; R Lüboldt, *Journ. prakt. Chem.* (1), **77**. 315, 1859: G. Bruhns, *Zentr. Zuckerind.*, **14**. 968, 1906; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **31**. 502, 1883; C. Meincke and K. Schröder, *Zeit. öffent. Chem.*, **3**. 5, 1897; F. Simond (*Dingler's Journ.*, **248**. 518, 1883) coats the store bottle with black varnish on the outside in order to protect the contents from light.

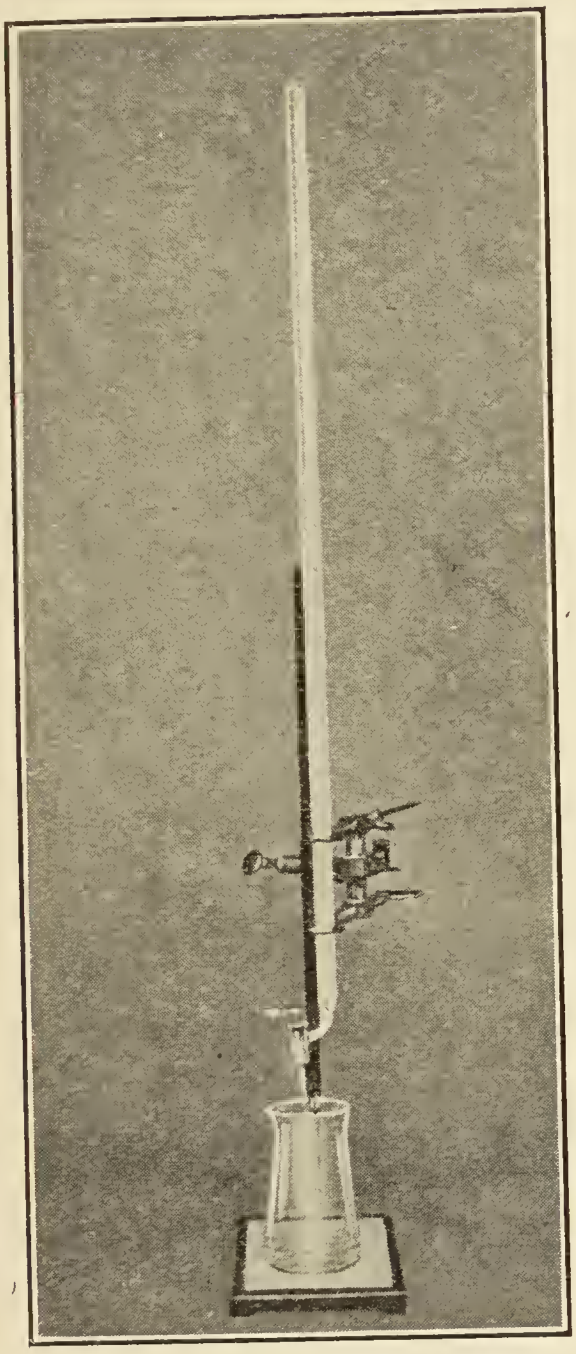

FIG. 105.—Burette for permanganate solutions.

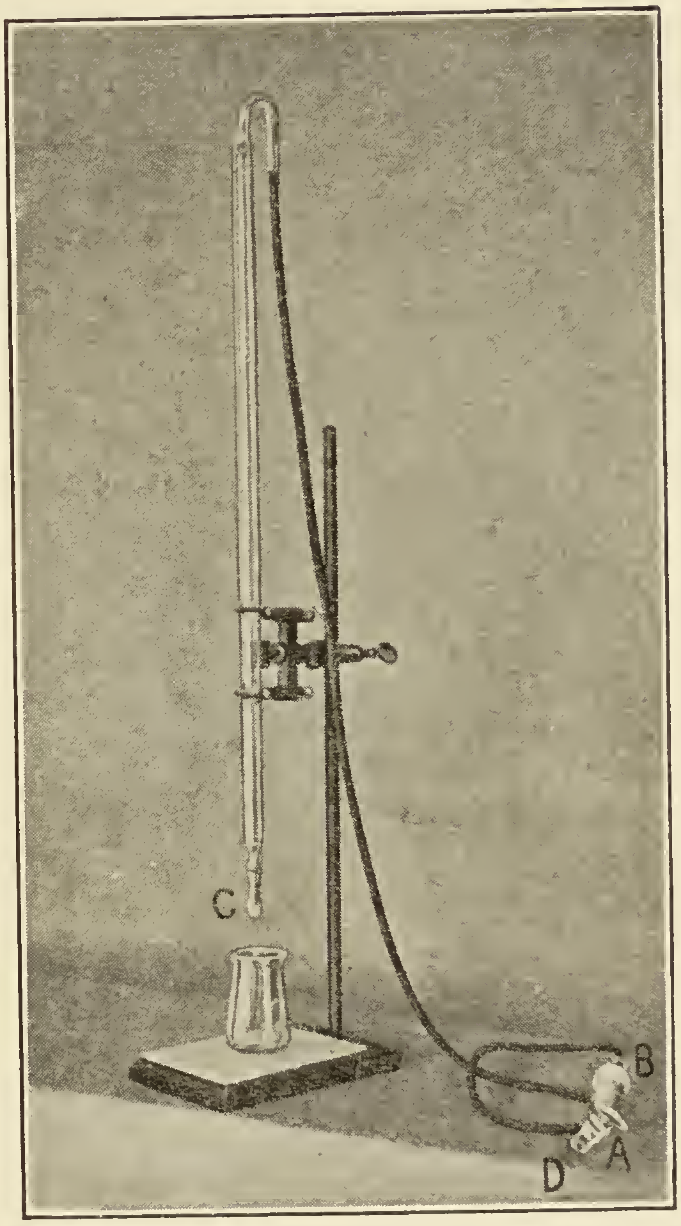

FIG. 106.—Scheibler's burette for permanganate solutions.

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[1] C. Scheibler, *Journ. prakt. Chem.* (1), **71**. 245, 1857; F. Stöber, *ib.* (1), **59**. 599, 1853; N. H. Darton, *Journ. Amer. Chem. Soc.*, **3**. 124, 1881; M. Kleinert, *Zeit. anal. Chem.*, **17**. 183, 1878; K. Abraham, *ib.*, **22**. 28, 1883; W. Alexandron, *ib.*, **49**. 436, 1910; T. H. Garret, *Chem. News*, **56**. 185, 1887; M. Heriot and R. Biggs, *ib.*, **26**. 189, 1872; E. Collens, *ib.*, **9**. 94, 1864; **26**. 203, 227, 1872; A. V. Harcourt, *ib.*, **26**. 239, 1872; C. Jones, *Journ. anal. Chem.*, **1**. 179, 1887; E. Hübner, *Rept. anal. Chem.*, **4**. 273, 1884; M. Vogther, *Archiv Pharm.* (3), **22**. 539, 189.

there is no danger of contamination by the lubricant of the stopcock. I prefer the ordinary glass-stoppered burette.

Burettes and other glass apparatus which have been used for permanganate solutions should be cleaned and rinsed immediately after use. Brown stains of manganese oxide can be removed by means of hydrochloric acid.

Calculations.—Obviously, if n c.c. of $KMnO_4$ are consumed in a titration, and w grms. of the clay are being investigated, the clay will contain $0{\cdot}0632n \div w$ per cent. of Fe_2O_3. The reaction between the permanganate and the ferrous salt is:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O.$$

EXAMPLE.—The results of the permanganate titration will be treated in the note-book somewhat as follows: 1 c.c. of the permanganate used represented 0·001510 grm. Fe_2O_3; 1 grm. of clay was treated; the reduction was complete after 10 grms. of zinc had been dissolved in the solution, and the solution required 13·84 c.c. of permanganate at 16°. In a blank experiment, 10 grms. of zinc dissolved in sulphuric acid required 0·51 c.c. of the permanganate solution. Hence, $13{\cdot}84 - 0{\cdot}51 = 13{\cdot}33$ c.c. represents the permanganate consumption by the iron salts in the gram of clay. This is equivalent to $13{\cdot}33 \times 0{\cdot}00151 = 0{\cdot}0201$ grm. Fe_2O_3; or the clay has 2·01 per cent. of Fe_2O_3. There was no need to apply the temperature correction.[1]

Temperature Corrections.—It is necessary to allow for the effect of variations of temperature exceeding ± 2° or ± 3° from the standard. Assume that the solution is standardised at 15°; then, if the solution be more concentrated than $\frac{1}{100}$N-$KMnO_4$, the correction table for water, page 29, may be applied. If the solution be between $\frac{1}{10}$N- and $\frac{1}{100}$N-$KMnO_4$, the following table may be employed:—[2]

Table XXXVI.—Temperature Corrections for Potassium Permanganate Solutions. (Standard temperature 15°.)

	0	1	2	3	4	5	6	7	8	9
0	...	...	...	...	...	+0·6	+0·6	+0·5	+0·5	+0·5
1	+0·4	+0·4	+0·3	+0·2	+0·1	0	−0·2	−0·3	−0·5	−0·6
2	−0·8	−1·0	−1·2	−1·4	−1·6	−1·8	−2·0	−2·3	−2·5	−2·8

The method of using the table will be obvious from the examples on page 30.

§ 91. The Volumetric Determination of Iron—Marguerite's Permanganate Process.[3]

Starting with the solution reduced by the ammonium bisulphite through which carbon dioxide is passing (page 192), remove and wash the carbon dioxide delivery tube—inside and out—into the flask with recently boiled distilled water.[1] Run in the standardised permanganate solution exactly as described in the preceding section, until a permanent pink blush is suffused throughout the liquid being titrated.[2] If desired, an allowance can be made if the vanadium be afterwards determined.

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[1] After the titration, the ferric oxide may be again reduced and the manganic oxide, if present, removed by filtration. The titration can thus be repeated until the volume of the liquid becomes unwieldy—B. Godwin, *Amer. J. Science* (2), **50.** 249, 1870; *Chem. News*, **22.** 269, 1870.

[2] The table may be also employed for N-, $\frac{1}{10}$N, and $\frac{1}{100}$N-solutions of sodium chloride; $\frac{1}{10}$N- and $\frac{1}{100}$N-solutions of silver nitrate; ammonium thiocyanate (1000 c.c. equivalent to 10 grms. Ag). The table is based on the work of A. Schulze (*Zeit. anal. Chem.*, **22.** 167, 1882), and may be modified for standard temperatures of reference other than 15°.

[3] F. Marguerite, *Compt. Rend.*, **22.** 587, 1846; *Ann. Chim. Phys.* (3), **18.** 244, 1846.

Errors.—The most frequent sources of error arise from the imperfect reduction of the ferric oxide and the deterioration of the permanganate. The latter difficulty is easily overcome by frequently standardising the permanganate; and the former by testing the solution for the presence of ferric salts before the reduction is stopped. Care must also be taken that no re-oxidation occurs before the titration. There is also a slight error due to the incomplete reduction of the permanganate, which was pointed out by Bray.[3] This occurs more particularly with low-temperature titrations, high acid concentration, and with a large volume of dilute solution. The conditions here recommended give most favourable results.

In illustration of the effect of titanium on the iron determination, and also in illustration of the magnitude of the errors which may be expected in the iron determination both by the ammonium bisulphite and the zinc reductions, the following data were obtained with eight independent analyses on one sample of clay. One gram of clay was taken for each determination, and the bisulphate fusion was divided into two equal portions, one reduced with zinc, and the other with ammonium bisulphite.

Table XXXVII.—Comparison of Zinc and Sulphite Reductions in the Permanganate Process for Iron in Clays.

Zinc reduction.		Ammonium bisulphite.	
c.c. $KMnO_4$.	Fe_2O_3.	c.c. $KMnO_4$.	Fe_2O_3.
6·92	0·0100	5·15	0·0078
6·85	0·0099	4·70	0·0069
6·84	0·0099	5·27	0·0079
6·32	0·0091	5·34	0·0076
6·61	0·0096	4·89	0·0073
6·09	0·0088	4·43	0·0068
6·49	0·0094	5·13	0·0077
6·19	0·0089	5·01	0·0075

The mean value for the ferric oxide with the zinc reduction is 0·0094, or 1·88 per cent., and with the bisulphite reduction, 0·0075, or 1·50 per cent., with a deviation of about ± 0·06.[4]

The clay contained 1·2 per cent. of titanium. If the clay contains vanadium, the V_2O_5 will also be reduced by the zinc to V_2O_3; and to V_2O_4 by sulphur dioxide (and possibly by hydrogen sulphide). The reduced oxides will be oxidised to V_2O_5 during the permanganate titration. The vanadium is, however, usually present in such small quantities that its influence can be neglected; see page 467.

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[1] If the solution has been reduced with zinc, with or without the bismuth oxide treatment, proceed with the titration as indicated in the text. It must be added that particles of filter paper may also reduce both permanganate and hot dichromate solutions, and thus lead to high results. The filter paper may get into the solution when the ammonia precipitate is dissolved in dilute acid, and titrated directly.

[2] The solution must not be too hot, or an excess of permanganate will be required. Some prefer to work with cold solutions; others with solutions between 60° and 70°. (Probably best —W. C. Bray, *Journ. Amer. Chem. Soc.*, **32.** 1204, 1910.) Whatever be the temperature employed, the conditions must be the same as those adopted in standardising the permanganate.

[3] W. C. Bray, *Journ. Amer. Chem. Soc.*, **32.** 1204, 1910; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2.** 498, 1911.

[4] The error is no greater, indeed less, if the whole of the sample be operated upon.

Correction with very Dilute Solutions.—If the amount of iron be small, permanganate containing half a gram per litre may be used. An error may now creep into the work owing to the fact that a certain quantity of permanganate is required to impart a perceptible colour to pure acidulated water. In such cases, the volume of the sodium oxalate used for the standardisation of the permanganate must be diluted to approximately the same volume as the solution containing the iron to be titrated, or the amount of permanganate required to impart the desired pink coloration to an equivalent volume of acidulated water must be determined, and the result deducted from the permanganate used in the titration.

The solution remaining after the permanganate titration can be used for the titanium determination, and afterwards for the determination of phosphorus.

§ 92. The Colorimetric Determination of Iron.

In 1853, Herapath[1] proposed to utilise the red colour produced when potassium or ammonium thiocyanate is mixed with a ferric salt for the determination of small quantities of iron.[2] According to Wagner,[3] this reaction enables 1 part of iron to be recognised in 1,600,000 parts of water. The colour is due to the formation of a double salt—$Fe(CNS)_3 . 9KCNS . 4H_2O$.[4] A large excess of potassium thiocyanate is needed to transform all the ferric salt into the thiocyanate and so produce the maximum coloration.[5] The intensity of the coloration is proportional to the amount of ferric thiocyanate in solution; hence, if a given solution containing a known amount of iron has the same colour as a solution containing an unknown amount of iron, it is inferred that both solutions have the same concentration, as indicated in discussing the principles of colorimetry, page 82.

Unfortunately, the intensity of the coloration of solutions of ferric thiocyanate is very sensitive to the presence of other salts in the solution.[6] In the case of dilute aqueous solutions the intensity of the coloration is not quite proportional to the amount of ferric thiocyanate present in the solution,[1] because some is hydrolysed by the solvent: $Fe(CNS)_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCNS$. Hence, when aqueous solutions are compared, the concentration of the solutions must be approximately the same. With the pyrosulphate fusion, in silicate analyses, the solutions have so nearly the same composition that the error from this cause can be regarded as negligibly small. Consequently, when but small quantities of iron are in question—up to 2 per cent.—the determination can be made much more conveniently by the colorimetric process than by gravimetric or volumetric methods.

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[1] T. L. Herapath, *Journ. Chem. Soc.*, **5**. 27, 1853; A. Thomson, *ib.*, **47**. 493, 1885; J. Davies, *Chem. News*, **8**. 163, 1863; A. Zega, *Chem. Ztg.*, **17**. 1564, 1862; F. Seiler and A. Verda, *ib.*, **26**. 803, 1906; L. Lapique, *Bull. Soc. Chim.* (3), **2**. 295, 1890; J. W. Leather, *Journ. Soc. Chem. Ind.*, **24**. 385, 1905; A. Jolles, *Arch. Hygiene*, **13**. 402, 1901; N. Damaskin, *Arbeit Pharm. Inst. Dorpat*, **7**. 40, 1891; J. W. Mellor, *Trans. Eng. Cer. Soc.*, **8**. 123, 1908; Hadank, *Sprech.*, **42**. 445, 1909; T. T. Morrell, *Amer. Chem.*, **4**. 287, 1874; H. P. T. Oerum, *Zeit. anal. Chem.*, **43**. 147, 1904; A. Jolles, *ib.*, **43**. 537, 1904; **44**. 6, 1905.

[2] H. B. Pulsifer (*Journ. Amer. Chem. Soc.*, **26**. 967, 1906) used the red colour of ferric acetylacetonate with excellent results; and A. Vogel (*N. Rep. Pharm.*, **25**. 180, 1876; S. Pagliani, *Gaz. Chim. Ital.*, **9**. 23, 1879; E. E. Smith, *Journ. Amer. Chem. Soc.*, **1**. 335, 1879), the red colour of ferric salts with salicylic acid. For the colours with ammonium sulphide, and with potassium ferrocyanide, see J. W. Mellor, *Trans. Eng. Cer. Soc.*, **8**. 123, 1909.

[3] A. Wagner, *Zeit. anal Chem.*, **20**. 349, 1881. E. E. Smith (*ib.*, **19**. 350, 1880) says 1 part in 8,000,000.

[4] G. Krüss and H. Moraht, *Liebig's Ann.*, **209**. 98, 1889; *Zeit. anorg. Chem.*, **1**. 399, 1893; A. Rosenheim and R. Cohn, *ib.*, **27**. 295, 1901.

[5] J. H. Gladstone, *Phil. Trans.*, **145**. 179, 1885; *Journ. Chem. Soc.*, **9**. 54, 1857.

[6] J. Pelouse (*Ann. Chim. Phys.* (1), **44**. 214, 1830) has shown that organic acids reduce the red colour very rapidly; also oxalates, citrates, tartrates, acetates, iodates, arsenates, phosphates, fluorides, and sulphates. Barium, strontium, and calcium chlorides exert a decolorising action (M. Vernon, *Chem. News*, **66**. 177, 191, 202, 214, 1892; J. H. Gladstone, *ib.*, **67**. 1, 1893; A. Dupré, *ib.*, **32**. 15, 1875; A. J. Shilton, *ib.*, **50**. 234, 1884; H. Werner, *Zeit. anal. Chem.*, **22**. 44, 1883); alumina also retards the development of the colour (R. R. Tatlock, *Journ. Soc. Chem. Ind.*, **6**. 276, 352, 1887); and generally, the colour obtained with a given proportion of iron depends upon the nature of the substances present in the same solution.

Test Solution.—Make the pyrosulphate fusion up to 250 c.c. with water. Pipette 25 c.c. into a 250-c.c.[2] flask, and make the solution up to the mark with water. Pipette 5 c.c. of this solution into the test cylinder; add 5 c.c. of potassium thiocyanate solution,[3] and add 20 c.c. water. The cylinder[4] then contains 30 c.c. of solution.

Standard Solution.—Pipette 5 c.c. of potassium aluminium sulphate solution[5] into the second test glass of the colorimeter; add 5 c.c. of potassium thiocyanate solution; and pipette 20 c.c. distilled water into the cylinder.

The Comparison.—Arrange the colorimeter (Weller's), burette, etc., as indicated in fig. 107. Fill a 10-c.c. burette, reading to $\frac{1}{50}$ c.c., with the standard ferric oxide solution,[6] and add the solution drop by drop to the standard cylinder in the colorimeter until the two tints are the same. The contents of the cylinder are stirred after every addition of 0·1 c.c. added from the burette, and for every addition from the burette, add an equal amount of water to the test cylinder, so that the conditions for the distribution of the red ferric thiocyanate may be approximately the same in both cylinders. If more than 3 or 4 c.c. of the standard ferric oxide solution are required the results will be inexact, because it is difficult to determine the changes of tint with concentrated solutions of ferric thiocyanate. In that case, the test solution was not sufficiently diluted, and another start must be made with a more dilute solution.

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[1] J. Riban, *Bull. Soc. Chim.* (3), **6.** 916, 1892; G. Krüss and H. Moraht, *l.c.*; A. Rosenheim and A. Cohn, *Zeit. anorg. Chem.*, **27.** 280, 1901; H. Schultze, *Chem. Ztg.*, **17.** 2, 1893; H. Ley, *Zeit. phys. Chem.*, **30.** 193, 1899; G. Magnanini, *ib.*, **8.** 1, 1891; L. Andrews, *Proc. Iowa Acad. Sciences*, **1.** 4, 1894; C. Féry and E. Tassilly, *Bull. Sci. Pharm.*, **19.** 11, 1912; E. Tassilly, *Bull. Soc. Chim.* (4), **13.** 34, 1913; O. Mayer, *Monit. Scient.* (5), **3.** 81, 1913. In order to eliminate the variable effects produced by the presence of other substances in the same solution, Tatlock (*l.c.*) proposed to compare the tints of the ethereal extract of the ferric thiocyanate, since J. Natanson (*Liebig's Ann.*, **130.** 246, 1864; C. Claus, *ib*, **99.** 51, 1856; W. Skey, *Chem. News*, **16.** 201, 324, 1867) has shown that, under these conditions, the reaction is more sensitive and less affected by the composition of the aqueous solution—G. Lunge, *Zeit. angew. Chem.*, **10.** 3, 1896; H. von Keler and G. Lunge, *ib.*, **8.** 669, 1894; A. Seyda, *Chem. Ztg.*, **22.** 1086, 1891; H. Lachs and H. Friedenthal, *Biochem. Zeit.*, **32.** 130, 1911. For similar reasons, W. M'Kim Marriott and C. G. L. Wolf (*Journ. Biol. Chem.*, **1.** 451, 1905; J. W. Gregory, *Proc. Chem. Soc.*, **23.** 306, 1907) used acetone; and H. N. Stokes and J. R. Cain (*Bull. Bur. Standards*, **3.** 115, 1907), a mixture of ether and isoamyl alcohol—2 : 5.

[2] The dilutions must be modified to suit the iron content of the clay, etc. For white burning clays, make 25 c.c. up to 250 c.c., that is, equivalent to making the whole clay up to 2500 c.c. Cream-coloured calcined clays may require 10 c.c., making up to 250 c.c.; this is equivalent to making the whole clay up to 6250 c.c. Red burning clays may require 5 c.c., making up to 250, 500, or 1000 c.c.

[3] POTASSIUM THIOCYANATE SOLUTION.—Dissolve 97 grms. of the recrystallised salt, free from iron, in a litre of water. For potassium chloride impurity, see J. Hendrick, *Chem. News*, **63.** 130, 1891.

[4] Smaller cylinders may be used than those indicated for Weller's colorimeter, page 84. Cylinders with a square cross section, 2·5 cm. side and 8 cm. high, are convenient.

[5] POTASSIUM ALUMINIUM SULPHATE SOLUTION.—Fuse 0·05 grm. of iron-free alumina with 5 grms. of potassium pyrosulphate until all is dissolved. Treat the solution as indicated for the pyrosulphate fusion, page 184. When the solution is made up to a litre, the amount used here should be such as to make the concentration of the solution of potassium aluminium sulphate in the two test cylinders of the colorimeter nearly the same.

[6] FERRIC OXIDE SOLUTION.—Dissolve 0·6303 grm. of ferric potassium alum—$Fe_2(SO_4)_3 . K_2SO_4 . 24H_2O$ (molecular weight 1006·56)—in water, add 5 c.c. concentrated sulphuric acid, and, when cold, make the solution up to a litre. One c.c. of this solution represents 0·0001 grm. of Fe_2O_3. This solution will keep indefinitely, under conditions where more dilute solutions would hydrolyse and deposit a brown oxide on the glass. For use, pipette 5 c.c. into a 100-c.c. flask, and make the solution up to the mark with distilled water; 1 c.c. has 0·000005 grm. Fe_2O_3, or 0·005 mgrm. Fe_2O_3—W. French, *Chem. News*, **60.** 235, 1889; L. L. de Koninck, *Bull. Soc. Chim.* (3), **23.** 261, 1909.

Two cubic centimetres of the standard iron solution may be run into the test cylinder and the standardisation repeated; or, another determination may be made *de novo*. It is well to take the mean of at least three determinations.

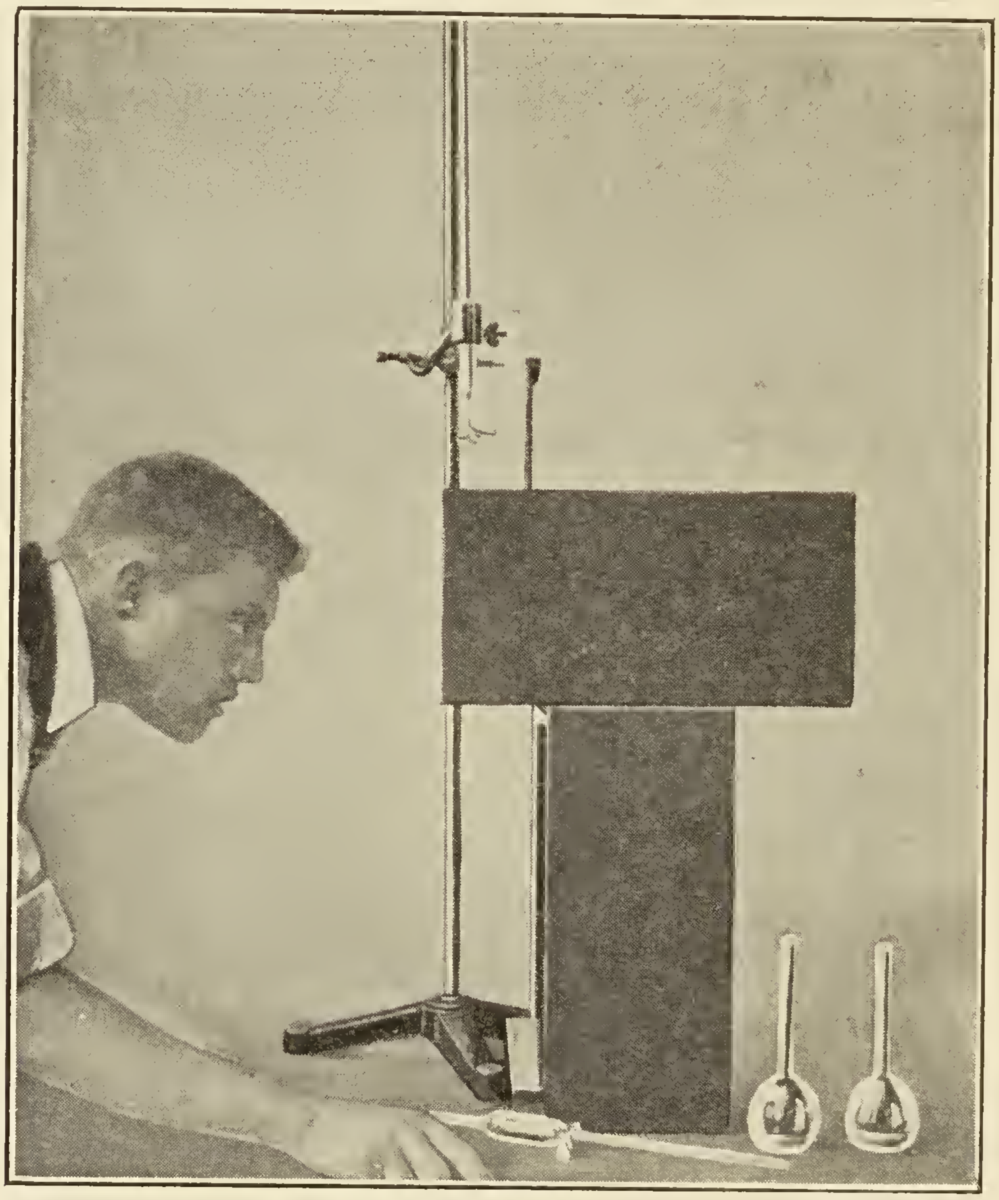

Fig. 107.—Colorimetric determination of iron.

Examples.—(1) The bisulphate fusion was made up to 250 c.c.; 25 c.c. of this were made up to 250 c.c., that is, equivalent to making the iron in the whole clay up to 2500 c.c. 5 c.c. of this solution required 2·24 c.c. of standard ferric oxide solution to give uniformity of tint. Hence, since 2·24 c.c. of the standard iron solution have the equivalent of 0·005 × 2·24 = 0·0112 mgrm. per 5 c.c., the 5 c.c. of the test solution had 0·0112 mgrm. of ferric oxide; hence, 2500 c.c., or 1 grm., of clay had 0·0112 × 500 = 5·6 mgrms. = 0·0056 grm.—that is, 0·56 per cent. Fe_2O_3.

(2) The bisulphate fusion was diluted to 250 c.c., and 5 c.c. were made up to 500 c.c. This is equivalent to diluting the "iron" in the gram of clay to 25,000 c.c. 1·74 c.c. of the ferric oxide were required to match the tint. This corresponds with 0·005 × 1·74 = 0·0087 mgrm. of Fe_2O_3 per 5 c.c. of test solution. Consequently, 25,000 of test solution would have 43·5 mgrms., or 0·0435 grm., of Fe_2O_3. Hence, the clay has 4·35 per cent. Fe_2O_3.

CHAPTER XV.

THE DETERMINATION OF TITANIUM.

§ 93. Weller's Colorimetric Process.

Scheerer[1] and Riley have emphasised the almost ubiquitous occurrence of titanium in silicate rocks. The quantitative separation of titanium from ferric oxide and alumina is not particularly difficult, but the process is somewhat tedious and laborious. The most important sources of error are due to (1) the tendency of the ferric oxide and alumina to separate with the titanium; (2) the presence of phosphoric acid hindering the complete precipitation of the titanium; (3) mechanical losses owing to the adhesion of the precipitated titanium oxide to the sides of the beaker;[2] and (4) the escape of some of the very finely divided precipitate through the pores of the filter paper. The colorimetric process is usually more convenient.[3]

A solution of titanium sulphate produces an orange-yellow colour when oxidised with hydrogen peroxide.[4] The intensity of the coloration depends upon the proportion of titanium present. If, therefore, a solution containing a known amount of titanium has the same tint as another solution of equal depth of liquid, it is assumed that both solutions contain the same proportion of titanium. Hydrogen peroxide is therefore added to the solution under investigation, and both the test and the standard solutions containing a known amount of titanium are systematically diluted until both solutions have the same tint.[5]

The presence of fluorine leads to low results, because fluorine partially bleaches the yellow colour produced by hydrogen peroxide. For instance, with solutions containing 0·01 grm. of titanic oxide:

Hydrofluoric acid . . .	0	0·00039	0·00194	0·0039	grm.
Titanic oxide	0·01	0·0093	0·0080	0·0068	grm.

Steiger[6] has proposed a colorimetric process for fluorine based on this property.

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[1] T. Scheerer, *Liebig's Ann.*, **92.** 178, 1854; *Chem. News*, **1.** 143, 1860; E. Riley, *Journ. Chem. Soc.*, **12.** 13, 1860.

[2] From which it can only be removed by the action of a solvent—say, conc. potash lye.

[3] Note, if the filtrate from the silica was treated with hydrogen sulphide, some titanium will be precipitated by the hydrogen sulphide.

[4] H. Schönn, *Zeit. anal. Chem.*, **9.** 41, 330, 1870; **8.** 380, 1869; V. Lehner and W. G. Crawford (*Jour. Amer. Chem. Soc.*, **35.** 138, 1913) recommend thymol; H. J. H. Fenton (*Journ. Chem. Soc.*, **93.** 1064, 1908) dihydroxymaleic acid—page 468.

[5] A. Weller, *Ber.*, **15.** 2599, 1882; C. Baskerville, *Journ. Soc. Chem. Ind.*, **19.** 419, 1900; J. Brakes, *ib.*, **20.** 23, 1901; H. M. Ullmann and J. W. Boyer, *Chem. Eng.*, **10.** 163, 1909; A. Gautier, *Chim.*, **1.** 177, 1910; *Rev. gén. Chim.*, **14.** 14, 1910; G. P. Pamfil, *Monit. Scient.* (4), **24.** 643, 1911.

[6] T. B. Osborne, *Amer. J. Science* (3), **30.** 329, 1885; *Chem. News*, **53.** 43, 1886; W. F. Hillebrand, *ib.*, **72.** 158, 1895; *Journ. Amer. Chem. Soc.*, **17.** 718, 1895; J. H. Walton, *ib.*, **29.** 481, 1907; G. Steiger, *ib.*, **30.** 219, 1908; H. E. Merwin, *Amer. J. Science* (4), **28.** 119, 1909; E. Jackson, *Chem. News*, **47.** 157, 1883; L. Levy, *Compt. Rend.*, **105.** 754, 1888; C. Reichard, *Chem. Ztg.*, **28.** 16, 1904.

The presence of phosphoric acid bleaches the colour and leads to low results. For instance, with solutions containing the same amount of titanium oxide, 0·01 grm., and

Phosphoric acid	0·00	0·13	0·26	0·52	0·78	1·04	1·30	grm.
Titanic oxide	0·0100	0·0090	0·0083	0·0074	0·0069	0·0066	0·0064	grm.

Potassium sulphate also weakens the tint produced by the titanium oxide, unless an excess of sulphuric acid be present.[1] For instance, with 6 grms. of potassium sulphate in each of three solutions containing the same amounts of titanium and hydrogen peroxide, Merwin found that with

H_2SO_4	0·4	2·9	8·0	c.c.
Bleaching	21	14	5	per cent.

From which it follows that, the greater the excess of sulphuric acid, the less the bleaching action.

Owing to the fact that the test solution obtained in the above analytical scheme contains the potassium sulphate used in the pyrosulphate fusion, an equivalent amount of potassium sulphate can be added to the standard solution in order that the comparison of tints can be made under similar conditions. In the same way, if the test solution contains appreciable quantities of phosphoric acid, an equivalent amount of phosphoric acid can be added to the standard solution.

A solution of ammonium molybdate in nitric acid,[2] as well as uranium and vanadium salts,[3] gives somewhat similar tints, and hence these salts, with the chromates, should be absent. The influence of iron salts will be discussed later.

The colorimetric process works well with quantities of titanium up to about 4 per cent. There is a wide range over which the colorimetric process is accurate. For titanium this ranges between concentrations represented by 0·0015 and 0·0200 grm. per 100 c.c. According to Wells,[4] the change in concentration required to produce a perceptible difference in the intensity of the colour of two solutions is about 6·5 per cent. The error is greater with weaker solutions, although by increasing the thickness of the layer of liquid [5] satisfactory comparisons can be made with solutions containing less than 0·0015 grm. of titanium per 100 c.c. Solutions more concentrated than 0·0200 grm. per 100 c.c. are not suited for colorimetric work. With the exercise of the greatest care, the accuracy of the colorimetric process for titanium is about 2 per cent. If more than 4 per cent. of titanic oxide be present, which is rarely the case with clays, the gravimetric process is best employed. More accurate results are obtained with colours not too intense. Colours approximating a deep straw yellow give the best results. The eye is not so sensitive to the small differences of tint in concentrated solutions. The left eye is usually rather more sensitive than the right eye. Better results are obtained after the eye has had a little practice with test solutions of known strength. *Cf.* p. 85.

Preparation of the Test Solution.—If necessary, evaporate the aqueous solution of the pyrosulphate fusion, acidified with sufficient sulphuric acid[1] to make the solution between 15 and 17 per cent. of H_2SO_4, that is, 9 c.c. of sulphuric acid per 100 c.c. If insufficient sulphuric acid be present the results are generally low. When the solution occupies about 150 or 200 c.c., cool. Transfer to, say, a 250-c.c. flask. Add enough hydrogen peroxide[2] to oxidise all the titanium in the solution. In general, 5 to 10 c.c. of hydrogen peroxide (20 vols.) suffice for 0·5 to 2 per cent. of titanium oxide. Make the solution up to 250 c.c. with distilled water.[3] Pour a part of this solution into the left cylinder of the colorimeter.

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[1] According to G. Steiger (*l.c.*), sodium salts give too high results.

[2] H. Schönn, *Zeit. anal. Chem.*, 9. 41, 330, 1870; H. Berwald, *Ber.*, 18. 1206, 1885; M. Fairley, *Journ. Chem. Soc.*, 31. 127, 1877; J. Aloy, *Bull. Soc. Chim.* (3), 27. 734, 1903; *Chem. News*, 87. 102, 1903.

[3] G. Werthier, *Journ. prakt. Chem.* (1), 83. 195, 1861; E. Jackson, *Chem. News*, 47. 157, 1883. Uranium salts (M. Fairley, *Journ. Chem. Soc.*, 31. 127, 1877) give a yellow colour with hydrogen peroxide.

[4] R. C. Wells, *Journ. Amer. Chem. Soc.*, 33. 504, 1911.

[5] In colorimeters of the type of Duboscq's (page 82).

Preparation of the Standard Solution.—Pipette, say, 5 c.c. of the standard solution[4] of titanium sulphate, containing, say, 1 grm. per litre, into a 100-c.c. flask; add 5 c.c. of hydrogen peroxide,[5] and make the solution up to 100 c.c.[6] Each cubic centimetre is then equivalent to 0·0001 grm. of TiO_2. Put, say, 10 c.c. of this standard solution into the right glass cylinder of the colorimeter, and 50 c.c. of water into a burette.[7] Add water to the solution until the colour of the standard is the same as the colour of the test solution in the left cylinder of the colorimeter. Note the amount of water added. The disposition of the colorimeter will be apparent from fig. 103. The sliding door of the colorimeter, glass stirring rod, burette with water, etc., are shown in the diagram.

Readings and Calculations.—The test solution was made up to 250 c.c. This was derived from 1 grm. of clay. 10 c.c. of the standard titanium solution containing 1 grm. of TiO_2 per litre were made up to 100 c.c. The 10 c.c. required 11·2, 11·3, 11·5, mean 11·33 c.c. of water to match the test solution. The 10 c.c. of the standard solution contained 0·01 grm. of TiO_2, and when diluted to 100 c.c., 10 c.c. of the diluted solution contained 0·001 grm. TiO_2. Hence, $10 + 11·33 = 21·33$ c.c. contained 0·001 grm. TiO_2; hence, 250 c.c. would have

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[1] To transform any basic titanium sulphates formed during the fusion into normal sulphate, and to counteract bleaching by potassium sulphate. P. Faber, *Chem. Ztg.*, **31**. 263, 1906; *Zeit. anal. Chem.*, **46**. 277, 1907; F. P. Dunnington, *Journ. Amer. Chem. Soc.*, **13**. 210, 1801.

[2] Hydrogen Peroxide.—This must be free from all traces of fluorides and phosphoric acid. Merck's perhydrol, containing 30 per cent. H_2O_2 by weight, is excellent when diluted. Make, say, 20 c.c. of perhydrol up to 100 c.c. with distilled water for a 6 per cent. (or 20 vol.) solution. The solution keeps better if acidified with, say, sulphuric acid. The general *rule for dilution* is: n volumes of perhydrol made up with water to 10 volumes furnishes, approximately, a $3n$ per cent. H_2O_2, or a $10n$ volume, solution. See pages 177 and 322.

[3] If the colorimetric process for iron has been used, this simply means adding the hydrogen peroxide, etc., to an aliquot portion of the pyrosulphate fusion.

[4] Standard Solution of Titanium Oxide.—Digest between 0·6 and 0·7 grm. of feebly calcined potassium titanofluoride—K_2TiF_6—in a platinum dish, with concentrated sulphuric acid, and evaporate until white fumes are evolved. Repeat the treatment three times, so as to drive off all the fluorine. Take up the residue with a little concentrated sulphuric acid and dilute until the solution has between 5 and 10 per cent. of sulphuric acid. Make up the solution to about a litre. Take two aliquot portions, between 50 and 100 c.c., dilute with water, heat to boiling, and precipitate the titanium hydroxide by the addition of ammonia. Wash the precipitate with hot water until free from alkalies, ignite for TiO_2, blast, and weigh. Duplicate determinations should be concordant. The solution may be diluted until it contains exactly 1 grm. of TiO_2 per litre. The solution should be kept in a bottle with a glass stopper coated with vaseline. Withdraw the amount needed for a determination by means of a pipette. Do not pour the solution from the bottle. See page 644 for an alternative process.

[5] The solutions should always be freshly prepared for an observation in both the test and standard cylinders.

[6] As much potassium sulphate as is present in the test solution may be added to the flask before making up with water to 100 c.c. Suppose that the 250 c.c. of the test solution was derived from the fusion of the ammonia precipitate with 6 grms. of potassium pyrosulphate $K_2S_2O_7$, the 250 c.c. will contain the equivalent of $0·7 \times 6 = 4$ grms. of K_2SO_4 per 250 c.c. Hence, approximately 20 c.c. of a solution of potassium sulphate containing 80 grms. K_2SO_4 per litre will be needed. The same quantity of potassium sulphate is added per 100 c.c. of water from the burette.

[7] The test solution should have a paler tint than the standard before the latter is diluted from the burette. If the clay contained excessive amounts of TiO_2, it may be necessary to further dilute the test solution—say, 25 c.c. to 100 c.c., or the standard solution may be made more concentrated.

$$\frac{0·001 \times 250}{21·33} = 0·0117 \text{ grm. } TiO_2.$$

Consequently, 1 grm. of the clay has 0·0117 grm. TiO_2, or the clay contains 1·2 per cent.

Correction for Iron.—According to Faber, if much iron be present, the results may be too high, because the iron intensifies the colour of the test solution. Hillebrand deducts 0·02 per cent. from the final result for every 10 per cent. of iron oxide present.[1] Faber[2] recommends the addition of phosphoric acid to both the standard and the test solutions in order to neutralise the effect of iron. It is necessary to add the phosphoric acid to both solutions, because phosphoric weakens the yellow tint, and both solutions are then affected in the same way. 50 c.c. of phosphoric acid (sp. gr. 1·3) per 250 c.c. will usually suffice.

W. A. Noyes[3] adds approximately an amount of ferric ammonium alum[4] to the standard, equivalent to the amount of ferric oxide in the test solution. To allow for the presence of iron, therefore, first make an approximate determination of the titanium in the clay, and let a denote the final number of c.c. in the standard after dilution; b the number of c.c. of water used in diluting the standard; and p the amount of iron in the test solution in terms of Fe_2O_3 per c.c.; and x the amount of Fe_2O_3 to be added per c.c. of water used in diluting the standard in the final test. Hence, bx denotes the amount of ferric iron in the water used for diluting the standard solution; and $ap \div 250$ denotes the amount of ferric oxide in the a c.c. of test solution. Consequently,

$$bx = \frac{ap}{250}; \text{ or, } x = \frac{ap}{250b} \text{ of } Fe_2O_3 \text{ per c.c.}$$

The Fe_2O_3 is added as ferric ammonium sulphate. Since 160 of Fe_2O_3 is equivalent to 964 of ferric ammonium alum, every gram of ferric oxide corresponds with 6 grms. of ferric ammonium alum.

Gautier[5] recommends making up a permanent set of standard comparison tints from methyl orange dissolved in water; as a matter of fact this method is somewhat risky. Lovibond's tintometer offers some advantages in making up a standard comparison scale; see page 486.

Results.—To show the deviations which might be expected in titanium determinations, the following results were obtained in eight independent determinations of titanium in one sample of clay:—

0·0120; 0·0125; 0·0125; 0·0113; 0·0114; 0·0126; 0·0125; 0·0113,

with a mean value 0·0120, or 1·20 per cent. The deviations from the mean are approximately ± 0·07.

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[1] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 133, 1910.

[2] P. Faber, *Chem. Ztg.*, **31**. 263, 1906; J. H. Walton, *Journ. Amer. Chem. Soc.*, **29**. 481, 1907.

[3] W. A. Noyes, *Journ. Anal. App. Chem.*, **5**. 39, 1891.

[4] STANDARD IRON SOLUTION.—Dissolve 27·6 grms. of ferric potassium sulphate—iron alum—in 500 c.c. of water. Add 100 c.c. of concentrated sulphuric acid, and make the solution up to a litre. The solution may be standardised, if necessary, by titration (page 198). Ferrous salts may exert a bleaching action on the titanium colour.

[5] A. Gautier, *Chim.*, **2**. 2, 1911; *Rev. gén. Chim.*, **14**. 16, 1911. 1 grm. of methyl orange is dissolved in 500 c.c. of water; 10 c.c. of this solution are diluted to 200 c.c.; and the solution is matched with solutions containing known amounts of titanium. The standards can afterwards be preserved, for, according to Gautier, they do not fade.

§ 94. The Gravimetric Determination of Titanium—Gooch's Process.

Titanium can be separated from aluminium by the prolonged boiling of a slightly acid solution of the sulphate. Thus, Lévy found the amount of hydrolysis (*cf.* page 181) in solutions containing pure titanium sulphate partly "neutralised" with potassium hydroxide, and boiled for six hours :—

Table XXXVIII.—Effect of Sulphuric Acid on the Precipitation of Titanic Oxide.

Free H_2SO_4 per 100 c.c.	Titanic oxide.	
	Used.	Precipitated.
0·000 *	0·086	0·108
0·000	0·086	0·100
0·000	0·036	0·047
0·083	0·036	0·036
0·500	0·086	0·085
1·000	0·082	0·086
5·766	0·030	0·000

* Slight excess of potassium hydroxide.

These results clearly show that if too much sulphuric acid be present, the titanium will be but imperfectly precipitated. If too little acid be present, some aluminium will be precipitated. Hence, the adjustment of the acidity of the solution is so difficult that the process is not at all satisfactory for general work.[1] Gooch's[2] method is based upon the solubility of alumina, and the insolubility of titanium hydroxide in solutions containing more than 5 per cent. of acetic acid by volume. The reaction is so delicate that Gooch obtained a distinct opalescence when 0·0005 grm. of titanic oxide was present in 500 c.c. of liquid containing in solution 10 grms. of alum and 15 grms. of sodium acetate, and 7 per cent. of acetic acid by volume. The process gives excellent separations of aluminium and titanium, but it does not work well in the presence of iron. The precipitation of basic ferric acetate will be prevented by the presence of 11 per cent. of acetic acid, yet "in the presence of a solution of ferric acetate, titanium shows a very marked tendency to remain dissolved." Thus, 400 c.c. of a solution of 10 grms. of sodium acetate, 17 per cent. of acetic acid, and the equivalent of 0·2 grm. of ferric oxide retained 0·06 grm. of titanium oxide in solution.[1] It is advisable to separate the iron as sulphide[2] from the mixture containing aluminium, iron, and titanium sulphates. The gravimetric determination involves four operations:—

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[1] L. Lévy, *Journ. Pharm. Chem.* (5), **16**. 56, 1887 ; *Ann. Chim. Phys.* (6), **25**. 433, 1892 ; H. Pellet and C. Fribourg, *Ann. Agron.* (2), **2**. 20, 1905 ; P. Holland, *Chem. News*, **59**. 27, 1889 ; D. Forbes, *ib.*, **19**. 3, 1869 ; J. Brakes, *Journ. Soc. Chem. Ind.*, **18**. 1097, 1899 ; C. Baskerville, *ib.*, **19**. 419, 1900. A. Leclerc (*Compt. Rend.*, **137**. 50, 1904) adds to an aqueous solution of the potassium bisulphate fusion enough formic acid to make the solution 5 per cent. acid. On standing two days at 100° all the titanic acid and silica are said to be precipitated.

[2] F. A. Gooch, *Proc. Amer. Acad. Science* (2), **12**. 435, 1885 ; *Amer. Chem. Journ.*, **7**. 283, 1885 ; *Chem. News*, **52**. 55, 68, 1885 ; T. M. Chatard, *ib.*, **63**. 269, 1891 ; *Amer. Chem. Journ.*, **13**. 106, 1891 ; B. Neumann, *Stahl Eisen*, **30**. 457, 1910 ; H. L. Vogt, *Zeit. prakt. Geol.*, **8**. 379, 1900 ; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 135, 1910 ; P. T. Austen and F. A. Wilber, *Amer. Chem. Journ.*, **5**. 389, 1883 ; *Chem. News*, **48**. 113, 1883 ; G. Werther, *Journ. prakt. Chem.* (1), **91**. 321, 1864 ; C. Baskerville, *Journ. Amer. Chem. Soc.*, **16**. 427, 1894 ; J. W. Bain, *ib.*, **25**. 1073, 1903 ; G. W. Wdowiszewski, *Eng. Min. Journ.*, **185**. 1200, 1908 ; W. M. Thornton, *Eng. Min. Journ.*, **94**. 353, 1912.

1. *Separation of Iron from Titanium and Aluminium.*[3]—The iron is best precipitated as ferrous sulphide from the feebly ammoniacal solution containing sufficient tartaric acid to keep the aluminium and titanium in solution. An amount of tartaric acid equal to three times the weight of the oxides to be held in solution is sufficient unless the ammonium salts be present in great excess. Hence, add, say, 0·7 grm. of tartaric acid to the solution;[4] reduce the iron to ferrous sulphide by means of hydrogen sulphide.[5] Add ammonia until the solution has cleared and the ammonia is in slight excess. Again pass hydrogen sulphide through the solution.[6] The clear supernatant liquid should not be tinted green,[7] though it might be slightly yellow. Filter the solution and wash the precipitate as quickly as possible in water containing ammonium sulphide in solution.[8] The precipitated iron may be dissolved in hydrochloric acid, boiled to expel hydrogen sulphide, oxidised with hydrogen peroxide, precipitated with ammonia, ignited, and weighed as Fe_2O_3.

2. *Decomposition of the Tartaric Acid.*[9]—The filtrate and washings may[10] be concentrated by evaporation, the solution acidified with sulphuric acid, and sufficient potassium permanganate added to leave the solution distinctly coloured after all the tartaric acid has been oxidised.[11] Generally, about 2·5 times the weight of the tartaric acid is needed.[12] If there be a deposit of manganese hydroxide formed, add sulphurous acid until it is dissolved.

3. *Separation of Titanium from Aluminium.*[3]—The solution may now contain manganese, aluminium, and titanium, together with some potassium sulphate. Add ammonia until the precipitate first formed dissolves with difficulty on stirring. If the precipitate does not dissolve, a drop or two of hydrochloric acid may be added. Add 20 grms. of sodium acetate and 7 to 10 c.c. of glacial acetic acid for every 100 c.c. of the solution under treatment (that is, about one-tenth the volume of the solution). Heat the solution to boiling and, after boiling one minute, let it stand a few more minutes to allow the flocculent precipitate of titanium hydroxide to subside. Decant the solution through a porous filter paper (*e.g.*, No. 589, Schlecher and Schull), and wash the precipitate first with 7 per cent. acetic acid, and finally with hot water. Dry the precipitate. Ignite 15 to 20 minutes over a Méker's burner. Cool, and weigh as TiO_2.

4. *Purification of the Titanium Oxide.*—The titanium oxide carries down

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[1] G. Streit and B. Franz, *Journ. prakt. Chem.* (1), **108**. 65, 1869.

[2] F. Reich, *Journ. prakt. Chem.* (1), **83**. 266, 1861; R. Fresenius, *Zeit. anal. Chem.*, **1**. 69, 1862.

[3] Also chromium. J. J. Berzelius, *Pogg. Ann.*, **4**. 3, 1825.

[4] Be careful to see that the tartaric acid is free from alumina.

[5] A. Cathrein (*Zeit. Kryst.*, **6**. 244, 1882; **7**. 250, 1883) recommends a repetition of process to recover traces of titanium precipitated with iron.

[6] Some platinum sulphide may separate. If so, filter and wash. The platinum crucible is slightly attacked during the bisulphate fusion.

[7] Showing that "ferrous" iron is still in solution.

[8] Keep the funnel covered with a clock-glass to prevent oxidation as much as possible, otherwise soluble ferrous sulphate may be formed.

[9] Enough sulphuric acid should be present to leave an excess after all the permanganate subsequently added has formed manganese sulphate. M. Dittrich and R. Pohl (*Zeit. anorg. Chem.*, **43**. 236, 1905) prefer oxidising the tartaric acid by evaporating to dryness, and digesting the residue with dilute sulphuric acid and potassium persulphate; W. M. Thornton (*Amer. J. Science* (4), **34**. 214, 1912) uses a mixture of sulphuric and nitric acids. See page 309.

[10] A. Fleischer, *Ber.*, **5**. 350, 1872; J. Hetper, *Bull. Acad. Science Cracow*, 601, 1910; L. Lindet, *Chem. News*, **76**. 212, 1897. See page 309.

[11] To carbonic and formic acids.

[12] Hence, in the example under consideration, about 0·7 × 2·5 = 1·8 grms. of potassium permanganate will be enough.

some manganese, alumina, alkaline sulphates, vanadic acid, etc. For exact work, therefore, the precipitate must be fused with about 10 times its weight of sodium carbonate[1] for about an hour over a blast. A residue of sodium titanate,[2] insoluble in water, remains; sodium phosphate, vanadate, and aluminate pass into solution. Filter and wash with water, containing a little sodium carbonate. Dry. Transfer the mass to a watch-glass. Ignite the filter paper in the crucible, and add the powder in the watch-glass to the ash. Fuse the contents with a little sodium carbonate. Cool. Dissolve the mass in 100 to 150 c.c. of water and add 20 c.c. of sulphuric acid. Nearly neutralise with ammonia as before and treat the solution with 5 grms. of sodium acetate and one-tenth its volume of glacial acetic acid. Boil one minute, filter, and wash as before. The fusions, precipitations, and ignitions should be repeated until the "titanium oxide" obtained is white in colour and constant in weight. Usually the two precipitations indicated above suffice. The purification of the precipitate does not take so long, because the precipitated titanium hydroxide is flocculent and filters easily. In illustration, the following results represent the weights obtained with a titaniferous bauxite:—

1st	2nd	3rd	4th	precipitation.
0·0752	0·0699	0·0694	0·0696	grm. TiO_2 obtained.

If zirconium be present, the titanium does not precipitate satisfactorily by this method, since, as Gooch has pointed out, the zirconium oxide acts in a similar manner to the ferric oxide mentioned above. Hillebrand[3] showed that 0·2 per cent of zirconia in a solution prevented the precipitation of 0·3 per cent. of TiO_2. Hence, Hillebrand recommends the removal of the zirconium as phosphate by the method indicated on page 498, before the titanium is determined.

§ 95. Blair's Modification of Gooch's Gravimetric Process.

If the amount of titanium is large, time can sometimes be saved by determining the amount of titanium in the original sample by Blair's process.[4]

Separation of Iron, etc.—Fuse, say, 1 grm. of the sample with 6–8 times its weight of sodium carbonate and a gram of sodium nitrite. Digest the cold mass with water. Filter off the insoluble residue which contains ferric oxide, sodium titanate, etc.[5] Dry and ignite the residue to burn off the filter paper.

Solution of Titanium Oxide.—Fuse the residue with 15–20 times its weight of potassium pyrosulphate. When cold, add 2–3 c.c. of concentrated sulphuric acid, and heat again until all is melted. Leave a piece of thick platinum wire in the fused mass. When cold, heat the crucible, to just soften the cake in contact with the crucible, and transfer the cake, by means of the piece of platinum wire, to a 600-c.c. beaker. Wash the crucible and lid with 5 per cent. sulphuric acid, and make the washings, etc., in the beaker to 150–200 c.c. with the 5 per cent. sulphuric acid.

Precipitation of Titanic Oxide.—Add 50 c.c. sulphurous acid.[6] Warm the solution, but not hotter than can be held comfortably by the hand. This accelerates the solution of the pyrosulphate cake, and the acid prevents the precipitation of the titanium at this temperature. If necessary, filter the solution from any silica which might separate. Add ammonia[1] until the precipitate which forms redissolves with difficulty.[2] Treat the solution with 10 c.c. of sulphurous acid, 20 grms. of sodium acetate dissolved in a little water, and one-sixth the total volume of the solution of acetic acid (sp. gr. 1·04, that is, about 49 per cent.). Heat the solution to boiling, and boil two or three minutes. Flocculent titanic oxide is precipitated. Digest the solution on a steam bath for half an hour.[3] Let the precipitate settle. Filter and wash first with hot water containing 5 per cent. of acetic acid, and finally with hot water. Dry the precipitate. If the precipitate is dark-coloured, instead of white, the titanic oxide may be contaminated with vanadic acid, etc.,[4] in addition to phosphoric acid, alumina, sulphates, etc. The precipitate is purified as indicated for Gooch's process, page 208.

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[1] A pink or green coloration is due to manganese.

[2] Iron oxide, if present, will also remain insoluble.

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 136, 1910.

[4] A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 184, 1908; F. J. Pope, *Trans. Amer. Inst. Min. Eng.*, **29**. 372, 1899; J. W. Bain, *Journ. Amer. Chem. Soc.*, **25**. 1073, 1903; J. J. Morgan, *Chem. News*, **75**. 134, 1897; G. B. Waterhouse, *ib.*, **85**. 198, 1902; E. Röer, *Chem. Ztg.*, **33**. 1225, 1909 (ilmenite); K. Borneman and H. Schirmeister, *Met.*, **7**. 71, 1911.

[5] Nearly all the phosphorus and aluminium pass into solution as sodium phosphate and aluminate. The filtrate may be used for the determination of other constituents—chlorine, fluorine, sulphur, etc. See pages 652, 637, 618, etc.

[6] Or 5 c.c. of a saturated solution of ammonium bisulphite.

§ 96. The Computation of the Results for "Alumina."

The analytical results may now be treated as follows:—

Crucible and ammonia precipitate	20·7003 grms.
Crucible alone	20·4520 ,,
Ammonia precipitate and silica residue	0·2483 grm.
Ash	0·0003 ,,
Alumina ferric oxide, titanic oxide, etc.	0·2480 grm.
Ferric oxide (p. 198)	0·0156 ,,
Titanic oxide (p. 204)	0·0120 ,,
Phosphoric oxide (p. 595)	0·0000 ,,
Manganese oxide (p. 372)	0·0000 ,,
Extra silica (p. 185)	0·0009 ,,
Sum	0·0285 grm.
Alumina, ferric oxide, etc.	0·2480 ,,
Sum of ferric oxide, etc.	0·0285 ,,
Alumina	0·2195 grm.

The eight alumina determinations in the clay mentioned above thus furnished:

0·2184; 0·2188; 0·2191; 0·2193; 0·2187; 0·2199; 0·2185; 0·2195

grm. Al_2O_3. The arithmetical mean is 21·90 per cent., and the deviations range between the limits ± 0·10. If the complete analysis proves faulty when submitted to the test mentioned on page 246, it will be generally found that the fault lies with the alumina determination.

In addition to the disturbing effects of phosphates and fluorides (discussed elsewhere) on the ammonia precipitate, the presence of borates and of oxalates may lead to the precipitation of the barium, strontium, calcium, and magnesium salts by ammonia; while the presence of citric and tartaric acids and sugars hinders or prevents the precipitation of iron, aluminium, and chromium.[5]

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[1] Or add a slight excess of ammonia, and then a few drops of sulphuric acid until the precipitate redissolves.

[2] If platinum is to be removed, the solution should be now treated with hydrogen sulphide.

[3] If filtered immediately, some titanium may be found in the filtrate.

[4] Iron, if present in the solution, would be carried down in the ferrous condition or as basic acetate.

[5] L. J. Cartman and H. Dabin, *Journ. Amer. Chem. Soc.*, 34. 1493, 1912.

CHAPTER XVI.

THE DETERMINATION OF CALCIUM AND MAGNESIUM.

§ 97. The Properties of Calcium Oxalate.

CALCIUM is precipitated from alkaline solutions as hydrated calcium oxalate—$CaC_2O_4.H_2O$—which is converted by calcination into calcium oxide—CaO. The calcium oxalate obtained by the first precipitation is so contaminated with sodium and magnesium salts that a second precipitation is advisable. If more magnesium than lime be present, the second precipitation is imperative; if not, one precipitation may be sufficiently exact for the purpose. In illustration, Fresenius[1] gives the following results:—

	Calcium oxide.		Magnesium oxide.	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.
One precipitation . .	0·2059	0·2063	0·4912	0·4904
Two precipitations . .	0·2051	0·2049	0·4927	0·4928

Hence, with one precipitation the lime was 0·0011 grm. (mean) too high, and the magnesia 0·0020 grm. (mean) too low.

Calcium oxalate is precipitated from feebly ammoniacal solutions, and also from solutions acidified with acetic acid,[2] oxalic acid, salicylic acid, or citric acid, by means of ammonium oxalate.[3] Ammonium chloride or sulphate,[4] or an excess of ammonium oxalate,[5] do not interfere very much, but in presence of ammonium salts the precipitate is said to be more difficult to filter. If, however, the precipitation be made in hot solutions, or in a solution acidified with acetic acid, the precipitate will be crystalline or granular, and filter easily.

Solubility.—The solubility of calcium oxalate in cold water is, for analytical purposes, negligibly small, but in hot water the solubility becomes appreciable,[1] particularly if the precipitate be subjected to a prolonged washing. The graph, fig. 108, shows the effect of temperature on the solubility of this salt in water. 100 c.c. of water at 95° will dissolve 0·0015 grm. of calcium oxalate, and at 18° 0·0007 grm. When first precipitated, calcium oxalate is more soluble than after standing some time, presumably owing to the fact that the fine particles grow into larger grains.[2]

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[1] R. Fresenius, *Zeit. anal. Chem.*, 7. 310, 1868; W. Gibbs, *Amer. J. Science* (2), 44. 213.

[2] *Chem. News*, 90. 248, 1904; W. Herz and G. Muhs, *Ber.*, 36. 3715, 1903.

[3] *Chem. News*, 90. 248. 1904; F. Utz, *Oester. Chem. Ztg.*, 7. 510, 1904.

[4] For the solubility of calcium oxalate in ammonium sulphate solutions, see R. Fresenius, *Zeit. anal. Chem.*, 30. 594, 1891.

[5] Zinc, barium, and lead, and also cobalt and nickel, if appreciable amounts be present, should be removed before adding the ammonium oxalate. Small quantities of nickel do not interfere when two precipitations are made. Uranium and arsenic do not interfere with the result. Manganese, copper, aluminium, molybdenum, and phosphoric acid, if present, will contaminate the precipitate more or less. Chromic acid does not interfere unless it has been reduced to chromic oxide by standing some time—*Chem. News*, 90. 248, 1904.

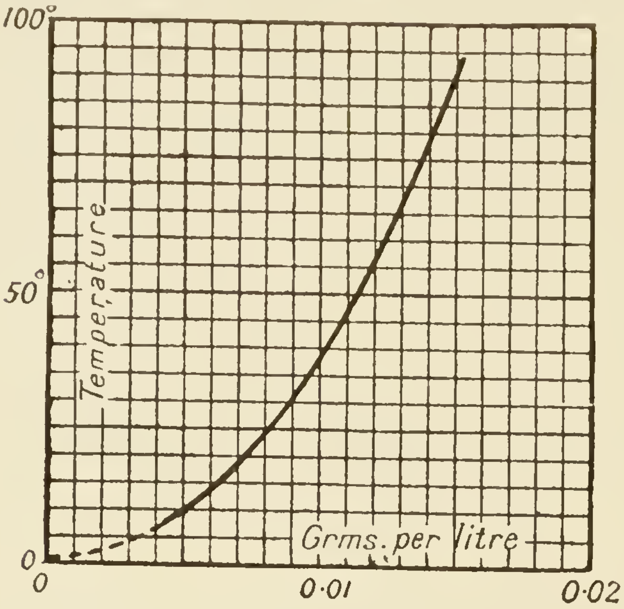

Fig. 108.—Solubility of calcium oxalate in water.

Influence of Magnesium.—A small proportion of magnesium salt accompanies the calcium oxalate precipitate even when a very large amount of ammonium chloride is present, and this particularly when the amount of magnesium is relatively large, or the amount of calcium oxalate relatively small. On the other hand, a certain amount of calcium escapes precipitation. Thus, if care be not taken in "separating calcium and magnesium, the result can only represent the truth by a fortuitous balancing of errors, the magnesium precipitated with the calcium compensating the calcium retained in the solution. When the calcium is reprecipitated two or three times, the result must be sensibly low."[3] This difficulty arises from the fact that calcium oxalate is soluble in magnesium chloride solutions, while magnesium oxalate is but slightly soluble in water. Hence, sufficient ammonium oxalate must be added to transform all the magnesium chloride into oxalate, and the solution must be so dilute that the magnesium oxalate remains in solution.[4] Free ammonia and warm solutions favour, and the presence of ammonium chloride retards, the precipitation of magnesium oxalate along with the calcium oxalate.[5] Hence, as recommended by Scheerer in 1859, two or three precipitations in the presence of a large excess of ammonium chloride are needed to get rid of the magnesium. Accordingly, many prefer to precipitate the "lime" as calcium sulphate by adding sodium sulphate and an excess of 90 per cent. alcohol, in which calcium sulphate is almost insoluble, while magnesium sulphate is fairly soluble in the same menstruum—see page 524.

Action of Heat.—Calcium oxalate, dried at 100°, has the composition $CaC_2O_4.H_2O$.[6] At 200° it loses water, forming CaC_2O_4; and at 500° it begins to decompose into calcium carbonate, with the separation of carbon. At the same time the carbon imparts a greyish colour to the mass. At a still higher temperature the carbon burns off, and the carbonate decomposes completely into calcium oxide—CaO—which remains as a white hygroscopic powder.

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[1] A. F. Holleman, *Zeit. phys. Chem.*, **12**. 125, 1893; F. Kohlrausch and F. Rose, *ib.*, **12**. 234, 1893; T. W. Richards, C. T. M'Caffrey, and H. Bislee, *Proc. Amer. Acad.*, **36**. 375, 1901; *Zeit. anorg. Chem.*, **28**. 71, 1901.

[2] W. H. Wollaston, *Phil. Trans.*, **103**. 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, **34**. 495, 1900; G. Hulett, *ib.*, **37**. 385, 1901; **47**. 357, 1904.

[3] T. Scheerer, *Journ. prakt. Chem.* (1), **76**. 424, 1859; G. C. Wittstein, *Zeit. anal. Chem.*, **2**. 318, 1863; E. Sonstadt, *Chem. News*, **11**. 97, 1865; **29**. 209, 1874; E. Divers, *ib.*, **11**. 144, 1865; M. Longchamp, *Ann. Chim. Phys.* (1), **12**. 255, 1819; E. Lenssen and A. Souchay, *Liebig's Ann.*, **99**. 31, 1856; **100**. 308, 1856; T. Scheerer, *ib.*, **110**. 236, 1859; H. Oeffinger, *Schweiz. Woch. Pharm.*, **6**. 265, 1868; F. Hundeshagen, *Zeit. öffent. Chem.*, **15**. 85, 1909.

[4] H. Hager, *Pharm. Centr.* (2), **6**. 226, 1865; **10**. 241, 1869.

[5] M. von Paguireff, *Journ. Russ. phys. Chem. Soc.*, **34**. 195, 1906. E. Murmann (*Zeit. anal. Chem.*, **49**. 688, 1910) says that "a good separation from magnesium is only possible by adding to the solution of the salts in 90 per cent. alcohol just sufficient sulphuric acid to form calcium sulphate, and washing with 90 per cent. alcohol." "The error is then within 0·15 per cent. of the true value; while the error in the oxalate method is from 0·5 to 2·0 per cent." A. Chizynski, *ib.*, **4**. 348, 1865.

[6] A. Souchay and E. Lenssen, *Liebig's Ann.*, **100**. 322, 1856.

§ 98. The Gravimetric Determination of Calcium.

If manganese has been determined, the filtrate from the manganese sulphide is boiled for an hour, and filtered from the precipitated sulphur;[1] and if manganese is not to be separated, the filtrate from the aluminium and ferric hydroxides is evaporated to about 300 c.c. The solution already contains considerable amounts of ammonium chloride; it should contain about 10 grms. per 100 c.c. of the solution per 0·0015 grm. of magnesia.

First Precipitation.[2]—Heat the solution to boiling, and add 2 c.c. of acetic acid per 100 c.c of the neutral solution. Meanwhile, say, 1 grm. of oxalic acid is dissolved in a little hot water, and added to the solution.[3] In about 5 minutes add a slight excess of ammonia. Let the solution cool for 2 or 3 hours. Pour the cold, clear solution through a 7-cm. filter paper. Wash three times by decantation with dilute ammonia (1 : 10), or a 1 per cent. solution of ammonium oxalate.

Second Precipitation.—The precipitate is contaminated with sodium and magnesium salts.[4] Dissolve the precipitate in dilute nitric acid (1 : 5), and collect the runnings in the same beaker in which the lime was first precipitated. About 50 c.c. of acid are needed. Tilt the beaker so that the acid wets the sides all round the beaker, in order to dissolve any adhering precipitate. Add a slight excess of ammonia and a few drops of oxalic acid solution. Boil. Allow to stand a couple of hours. When cold, filter[5] and wash as before. Transfer all the precipitate to the filter paper. The sides of the beaker will want carefully rubbing with the "policeman," since the precipitate adheres very tenaciously, and is sometimes difficult to see when wet.

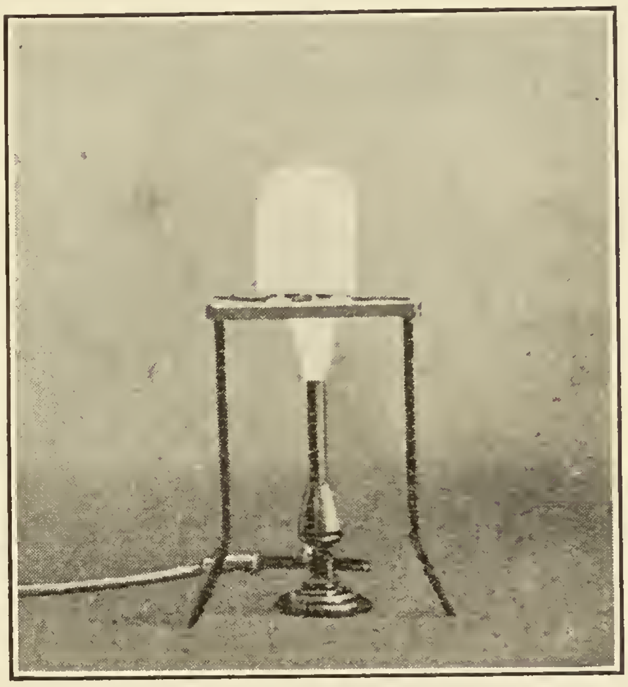

FIG. 109.—Winkler's chimney.

The Ignition of the Precipitate.—Place the moist filter paper in an ignited and weighed crucible. Heat gently so as to char the paper —fig. 96 or fig. 112. Incinerate the precipitate with the crucible inclined at an angle of, say, 45°, so as to burn the carbon mixed with the oxalate. Blast about 10 minutes, or heat over a Méker's or Teclu's burner with a Winkler's chimney (fig. 109),[6] so as to raise the temperature above that possible with an unprotected flame. Cool the crucible in a desiccator,[7] and weigh as quickly as possible to avoid the absorption of carbon dioxide and moisture[1] from the atmosphere. If the precipitate be large, ignite once again and reweigh in order to make sure that the conversion of the oxalate to oxide was complete.[2]

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[1] Note the possible formation of sulphuric acid, and precipitation of, say, barium as sulphate—C. de la Harpe, *Bull. Soc. Ind. Muhlhouse*, 245, 1885.

[2] E. Murmann, *Monats. Chem.*, **32**. 105, 1911; *Oester. Chem. Ztg.*, **12**. 305, 1909; *Zeit. anal. Chem.*, **49**. 688, 1910.

[3] At least four times as much ammonium oxalate is required beyond that needed to form calcium oxalate with the lime, and magnesium oxalate with the magnesia. Note that commercial ammonium oxalate sometimes contains calcium salts.

[4] T. Scheerer, *Journ. prakt. Chem.* (1), **79**. 424, 1859; A. Cossa, *Zeit. anal. Chem.*, **8**. 141, 1869; T. W. Richards, *Zeit. anorg. Chem.*, **23**. 383, 1900; W. C. Blasdale, *Journ. Amer. Chem. Soc*, **31**. 917, 1909; C. Stolberg, *Zeit. angew. Chem.*, **17**. 741, 769, 1903; R Hefelmann, *Zeit. öffent. Chem.*, **3**. 193, 1897; N. Knight, *Chem. News*, **89**. 146, 1904; C. Liesse, *Bull. Assoc. Chim. Sucr. Dist.*, **28**. 559, 1910; F. H. M'Crudden, *Journ. Biol. Chem*, **10**. 187, 1911.

[5] A Gooch's crucible may be used.

[6] O. Brunck, *Zeit. anal. Chem.*, **45**. 80, 1906. They are made by the Kgl. Sächs. Muldenhütte bei Freiberg i. S., and have proved very useful for general work in the laboratory.

[7] Containing concentrated sulphuric acid. According to O. Brunck (*Zeit. angew. Chem.*, **17**. 953, 1904), the oxide should be dried over sulphuric acid, because the carbon dioxide of the

Other Methods of Weighing the Precipitate.—Instead of weighing the calcium in the form of oxide,[3] some prefer to convert the oxalate into carbonate, or sulphate, or fluoride. The objection is made that in converting the oxalate into oxide the crucible loses weight during the 10 minutes' blasting,[4] and the oxide is difficult to weigh on account of its hygroscopicity. If small quantities are in question, it might be well to convert the oxalate into sulphate or fluoride. Care must then be taken to avoid loss by the spurting which will occur if the crucible be heated too rapidly.[5]

Transformation of Calcium Oxalate to Calcium Sulphate.—First ignite the oxalate at a comparatively low temperature, sufficient to burn the paper and convert most of the oxalate into oxide. Add one or two c.c. of water, gradually, drop by drop, to avoid spurting. This treatment will transform the calcium oxide into hydroxide. Add a slight excess of dilute sulphuric acid; drive off the excess with a small flame; and finally ignite the crucible at a dull red heat.[6] Weigh the resulting calcium sulphate—$CaSO_4$—and multiply the weight by 0·41195 in order to get the equivalent amount of CaO.

Souchay[7] examined the results obtained by weighing the lime as oxalate, as carbonate, as sulphate, and as caustic lime, with the following results:—

	Oxalate.	Carbonate.	Sulphate.	Oxide.	
CaO . . .	38·12	38·09	38·06	38·12	per cent.

Hence, it follows that, with care, all the methods furnish satisfactory results. In cases like this, where different methods furnish equally reliable results, the choice of any particular process is determined by convenience, risk of error, and time.

Errors.—The following numbers represent the results of eight independent determinations by the "oxalate to oxide" process on one sample of clay:—

0·0137; 0·0141; 0·0147; 0·0142; 0·0152; 0·0152; 0·0141; 0·0142;

with a mean value of 0·0145 grm. CaO corresponding with 1·45 per cent. CaO. The deviations from the mean are ± 0·08.

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air may lead to the evolution of chlorine by the calcium chloride. It might be questioned whether this action could affect the result appreciably.

[1] To illustrate the hygroscopicity of the powder, R. Fresenius (*Quantitative Chemical Analysis*, London, **2.** 633, 1900) states that 0·5599 grm. of calcium oxide weighed 0·5605 grm. after standing 2 minutes on the pan of the balance; 0·5609 grm. after standing 6 minutes; and 0·5625 grm. after standing 17 minutes.

[2] If the clay contains strontia, this will be precipitated with the lime. To remove the strontia, convert the precipitates to nitrates and digest the mixture with a mixture of absolute alcohol and ether (page 514). The calcium nitrate is washed away, and the insoluble strontium nitrate is ignited and weighed as SrO. The CaO is obtained by subtraction from the weight of mixed CaO + SrO.

[3] A. Fritzsche, *Zeit. anal. Chem.*, **3.** 177, 1864.

[4] O. Brunck, *Zeit. anal. Chem.*, **45.** 77, 1906.

[5] E. Kettler, *Zeit. angew. Chem.*, **17.** 685, 1904; O. Brunck, *ib.*, **17.** 953, 1904; E. Murmann, *Zeit. anal. Chem.*, **49.** 688, 1910; A. N. Clark, *Journ. Amer. Chem., Soc.*, **26.** 110, 1904. F. B. Guthrie and C. R. Barker (*Journ. Roy. Soc. N.S.W.*, **36.** 132, 1902) ignite the oxalate with ammonium nitrate equal to the bulk of the lime in the crucible; and W. H. Hess (*Journ. Amer. Chem. Soc.*, **22.** 477, 1900) then adds twice as much ammonium sulphate; ignites at a dull red heat; and weighs as calcium sulphate. A. Schrötter (*Die Chemie*, Wien, 2, 1849) uses ammonium sulphate alone. For the decomposition of calcium and magnesium sulphates by heat, A. Mitscherlich, *Journ. prakt. Chem.* (1), **83.** 485, 1861; J. Boussingault, *Compt. Rend.*, **64.** 1159, 1867; W. Schütz, *Metallurgie*, **8.** 228, 1910.

[6] The use of the ring burner, fig. 96, page 170, reduces to a minimum the risk of loss by spurting.

[7] A. Souchay, *Zeit. anal. Chem.*, **10.** 323, 1871; R. Fresenius, *ib.*, **10.** 326, 1871.

§ 99. The Volumetric Determination of Lime—Kraut's Process.

For routine work with calcareous clays, it is quickest to determine the lime volumetrically.[1] Spread the paper carrying the precipitated and washed calcium oxalate on the side of the beaker; and wash the calcium oxalate from the paper by means of a jet of hot water, and then with dilute sulphuric acid (1 : 4). Remove the paper, add sufficient water to make the solution up to about 50 c.c. Add 10 c.c. of concentrated sulphuric acid, and titrate the hot solution (60°-70°) with standard permanganate, as indicated for sodium oxalate (page 194), until the solution is tinged with a permanent pink colour.

The reaction which takes place during the titration is represented by the equation:

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + CaSO_4 + 8H_2O + 10CO_2.$$

This shows that 1 grm. of $KMnO_4$ corresponds with 0·887 grm. of CaO.

EXAMPLE.—One gram of the sample was taken. The permanganate solution used in a titration contained 2·4 grms. of $KMnO_4$ per litre, and 20·5 c.c. were used. Here 1 c.c. of the permanganate has 0·0024 grm.; hence, 20·5 c.c. have 0·0492 grm. of $KMnO_4$; and the sample contains $0·0492 \times 0·887 = 0·0436$ grm. CaO. The sample used for the analysis had 4·36 per cent. of calcium oxide—CaO. The method is not recommended when but a few determinations are made, and it is only used when a large number of analyses have to be conducted concurrently.

§ 100. The Properties of Ammonium Magnesium Phosphate.

A precipitate of ammonium magnesium phosphate is obtained in the determination of magnesia by adding a soluble phosphate to the ammoniacal solution containing the magnesium compound.

Composition of the Precipitate.—According to Neubauer,[2] the precipitation is practically complete, even in the presence of comparatively large quantities of ammonium salts, including the oxalate, but the composition of the precipitate is largely determined by the nature of the solution. The ammonium-magnesium phosphate may exist in three different forms, according to the composition of the mother liquid at the time of precipitation:—

1. In neutral or ammoniacal solutions, the precipitate is $Mg(NH_4)_4(PO_4)_2$. This contains less magnesium than the normal $MgNH_4PO_4$. The former compound, on calcination, decomposes, forming magnesium metaphosphate, water, and ammonia:

$$Mg(NH_4)_4(PO_4)_2 \rightarrow Mg(PO_3)_2 + 4NH_3 + 2H_2O.$$

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[1] W. Hempel, *Mémoires sur l'emploi de l'acide oxalique dans les dosages à liqueurs titrées*, Lausanne, 1853; K. Kraut, *Henneberg's Landwirthsch.* (1), **4.** 112, 1856; *Zeit. anal. Chem.*, **26.** 629, 1887; L. T. Bowser, *Journ. Ind. Eng. Chem.*, **3.** 82, 1911; G. P. Baxter and J. C. Zanette, *Amer. Chem. Journ.*, **33.** 500, 1905; H. Walland, *Chem. Ztg.*, **27.** 922, 1906; C. H. Schultze, *ib.*, **29.** 508, 1905; B. Enright, *Journ. Amer. Chem. Soc.*, **26.** 1003, 1904; T. Ulke, *Monit. Scient.* (4), **14.** 775, 1908; M. Kruger, *Zeit. physiol. Chem.*, **16.** 445, 1892; G. Lunge, *Zeit. angew. Chem.*, **17.** 265, 1904; J. Volhard, *Liebig's Ann.*, **198.** 333, 1879; E. Rupp and A. Bergdolt, *Archiv Pharm.*, **242.** 450, 1890; C. A. Peters, *Zeit. anorg. Chem.*, **29.** 145, 1902; H. M. Davy, *Chem. News*, **29.** 250, 1874; *Compt. Rend.*, **78.** 978, 1874; A. Heifer, *Tonind. Ztg.*, **18.** 535, 1894; K. von Radlowski, *ib.*, **18.** 592, 1894.

[2] H. Neubauer, *Ueber die Zuverlässigkeit der Phosphorsäurebestimmung als Magnesiumpyrophosphat*, Rostock, 1893; *Journ. Amer. Chem. Soc.*, **16.** 289, 1894; W. Heintz, *Zeit. Chem.*, (2), **6.** 479, 1870; O. Popp, *ib.* (2), **6.** 395, 1870; K. Bube, *Ueber Magnesiumammoniumphosphat*, Weisbaden, 1910; R. Reidenbach, *Ueber die quantitative Bestimmung dés Magnesiums als Magnesiumpyrophosphat*, Kusel, 1910.

On further calcination, the metaphosphate decomposes into magnesium pyrophosphate and phosphoric anhydride:

$$2Mg(PO_3)_2 \rightarrow Mg_2P_2O_7 + P_2O_5$$

and some phosphoric anhydride is volatilised.[1]

2. When an excess of magnesium salt is present, and no excess of ammonia, the precipitate has the normal composition—$MgNH_4PO_4$—and the results are correct.

3. If an excess of magnesium salt and an excess of ammonia be present, the precipitate contains more magnesium than the normal phosphate, and the calculated phosphoric acid will be too high.

Nerl has verified the first, and Reidenbach the second observation of Neubauer; but Reidenbach considers that the third observation is not correct. He found the precipitate contained less, not more, magnesium than Neubauer's statement represents.

In any case, it is necessary to precipitate the ammonium-magnesium phosphate in a solution containing definite amounts of ammonia, ammonium salts, magnesia, and phosphoric acid in order to obtain concordant results. The precipitant should also be added to the *acid* solution, and the ammonia in slight excess added *afterwards*.

Solubility of Ammonium-Magnesium Phosphate.—The precipitate is readily soluble in dilute acids, and 100 c.c. of water at 10° dissolve 0·0065 grm. of the salt. It is much less soluble in aqueous ammonia.[2] Thus, according to Stünkel, Wetzke, and Wagner, the amounts of ammonia indicated in the first line of the following scheme dissolve per litre:—

Ammonia	1	2	3	per cent.
MgO	0·00050	0·00023	0·00008	grm.
P_2O_5	0·00088	0 00038	0·00015	,,

The solubility of the ammonium magnesium phosphate in ammonia is also illustrated by graph, fig. 110, which shows that the solubility of normal ammonium magnesium phosphate decreases very rapidly with increasing concentration of ammonia.[3] According to Jorgensen, the solubility in 2·5 per cent. ammonia is approximately 0·00006 grm. of MgO per 100 c.c. This is negligibly small.[4] The solubility is increased in the presence of ammonium chloride, so that 0·0013 grm. is dissolved per 100 c.c. in the presence of 2·5 per cent. ammonia containing a gram of ammonium chloride. The effect of ammonium chloride on the solubility of the magnesium ammonium phosphate is illustrated by the graph, fig. 111.

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[1] D. Campbell, *Phil. Mag.* (4), **24**. 380, 1862.

[2] G. Jorgensen, *Mem. Acad. Roy. Soc. Danemark* (7), **2**. 141, 1905; C. Stünkel, T. Wetzke, and F. Wagner, *Zeit. anal. Chem.*, **21**. 353, 1882; T. R. Ogilvie, *Chem. News*, **31**. 274, 1875; **32**. 5, 12, 70, 1875; E. W. Parnell, *ib.*, **32**. 222, 1875; **23**. 145, 1871.

[3] According to A. Bolis (*Chem. Ztg.*, **27**. 1151, 1903), 2 grms. of $MgNH_4PO_4 . 6H_2O$ in contact with 100 c.c of a solution of ammonium citrate (400 grms. of citric acid per litre) loses, by solution, an average 0·457 per cent. in weight at ordinary temperatures, and 0·587 per cent. at 50°.

[4] There is therefore no need to correct for the solvent action of the wash liquids as recommended by C. R. Fresenius, *Anleitung zur quantitative chemischen Analyse*, Braunschweig, **1**. 333 1863; *Liebig's Ann.*, **55**. 111, 1845; R. Warington, *Journ. Chem. Soc.*, **18**. 27, 1865; W. Kübel, *Zeit. anal. Chem.*, **8**, 125, 1869; O. Abesser, W. Jani, Märcker, *ib.*, **12**. 239, 1873; F. A. Gooch, *Amer. Chem Journ.*, **1**. 391, 1879; T. S. Gladding, *Chem. News*, **46**. 213, 1882; **47**. 71, 1883. To get some idea of the effect of the solubility of the precipitate, three solutions containing the same amount of magnesia were treated in exactly the same manner, but the precipitates were respectively washed with a litre of 1, 2, and 3 per cent. ammonia. The corresponding precipitates gave 0·1956, 0·1967, 0·1968 grm. of ammonium magnesium phosphate. Theory required 0·1971 grm. Nothing like a litre of washing liquid is required in practice, so that the errors from this cause must be negligibly small.

The presence of ammonium chloride, curiously enough in view of fig. 111, furnishes precipitates with positive, not negative errors. Otherwise expressed, the results were too high. For example, in solutions containing

NH_4Cl	0	2·67	5·35	10·70	grms. per litre
$Mg_2P_2O_7$	0·5567	0·5603	0·5612	0·5619	grm.
Error	...	+0·0036	+0·0045	+0·0052	,,

The solution from which the magnesium phosphate is first precipitated usually contains not only ammonium chloride and ammonia, but also ammonium oxalate, and considerable amounts of sodium chloride. The effect of ammonium oxalate, like ammonium chloride, is to raise the weight of the precipitate above the normal. Thus, in solutions containing

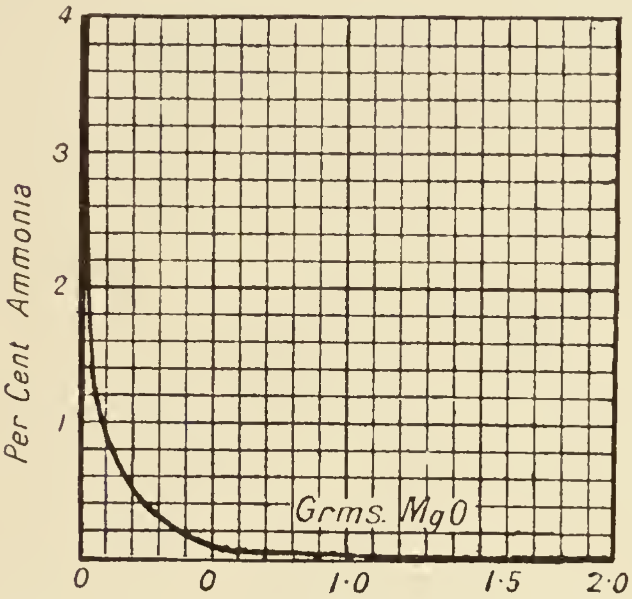

Fig. 110.—Effect of ammonia on the solubility of ammonium magnesium phosphate.

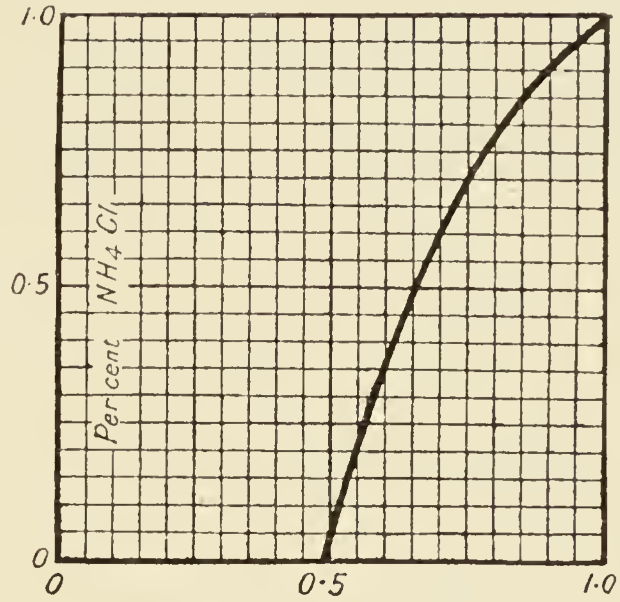

Fig. 111.—Effect of ammonium chloride on the solubility of ammonium magnesium phosphate.

$(NH_4)_2C_2O_4$	0	3·55	4·26	4·97	grms. per litre
$Mg_2P_2O_7$	0·5567	0·5900	0·5864	0·5863	grm.
Error	...	+0·0333	+0·0297	+0·0296	,,

The presence of sodium chloride in the mother liquid also considerably augments the weight of the resulting precipitate. Thus, in solutions containing

NaCl	0	0·585	5·85	23·4	grms. per litre
$Mg_2P_2O_7$	0·5567	0·5585	0·5689	0·5770	grm.
Error	...	+0·0018	+0·0122	+0·0203	,,

The effect with potassium chloride is much greater than with sodium chloride. The practical lesson to be learned from these observations is that *the magnesium ammonium phosphate first precipitated must be dissolved in dilute acid, and reprecipitated, otherwise the result will be of little value.*

The precipitate is more soluble in hot solutions. With hot solutions there is also a loss of ammonia. Hence, the precipitation should be made in cold solutions, with an excess of the precipitating agent, and in the presence of at least 2·5 per cent. of ammonia. The precipitate made in solutions containing ammonium salts—chloride and oxalate—and sodium chloride is very impure, and it must in consequence be dissolved in dilute acids, and reprecipitated as described below.

Action of Heat.—Ammonium magnesium phosphate—$MgNH_4PO_4.6H_2O$—loses $5H_2O$ at about 100°, and the remaining H_2O with the ammonia, at a red heat, forming magnesium pyrophosphate.

$$2MgNH_4PO_4.6H_2O \rightarrow Mg_2P_2O_7 + 2NH_3 + 14H_2O.$$

If the temperature be raised still further, the pyrophosphate becomes incandescent, owing to an intermolecular change—according to Popp,[1] a passage from the crystalline to an amorphous condition. The magnesium pyrophosphate fuses at 1220°. If magnesium pyrophosphate be exposed to a reducing atmosphere at a high temperature, phosphorus, phosphorus hydride, and phosphorus oxide are said to be volatilised.[2] These vapours attack the platinum crucibles. The pyrophosphate is soluble in dilute nitric and hydrochloric acid, and but sparingly soluble in water.

Precipitation of Ammonium Magnesium Phosphate for the Determination of Phosphorus.—An excess of magnesium chloride (magnesia mixture, page 597) reduces the solubility[3] of magnesium ammonium phosphate even more than an excess of the phosphate solution. No phosphoric acid, for example, could be detected in a filtrate which would, without the excess magnesium chloride, have contained the equivalent of 0·0025 grm. P_2O_5. An excess of a soluble phosphate also reduces the solubility of the ammonium magnesium phosphate in a similar manner.

§ 101. The Gravimetric Determination of Magnesia.

The magnesia is determined in the filtrate from the calcium oxalate by the addition of a soluble phosphate; a precipitate of ammonium magnesium phosphate separates. Unfortunately, the composition of the precipitate is considerably modified by the composition of the solution in which the precipitation takes place.[4] The precipitate is therefore redissolved, and reprecipitated under definite conditions whereby the precipitate $MgNH_4PO_4$ is obtained. This is ignited and weighed as $Mg_2P_2O_7$.

First precipitation.—Gradually add a solution containing, say, 2 grms. of sodium ammonium phosphate[5] (dissolved in 15 c.c. of water) to the solution under investigation,[6] with constant stirring. While still stirring the solution,[1] gradually add, drop by drop, about one-third its volume of aqueous ammonia; cover the solution with a watch-glass,[2] and let it stand 12–24 hours.[3] Filter. Wash the precipitate with dilute ammonia (1 : 10, that is, about 2·5 per cent.).[4] Reject the filtrate, which should give a precipitate with "magnesia mixture" (page 597). When the washing is completed, the runnings will give no precipitate with silver nitrate in acid (HNO_3) solution. Reject the filtrate and washings.

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[1] O. Popp, *Zeit. anal. Chem.*, **13**. 305, 1874.

[2] H. Struve, *Journ. prakt. Chem.* (1), **79**. 349, 1860; R. Weber, *Pogg. Ann.*, **73**. 146, 1848.

[3] W. Heintz, *Zeit. anal. Chem.*, **9**. 16, 1870; E. Kessel, *ib.*, **8**. 173, 1869; W. Kübel, *ib.*, **8**. 125, 1869; R. Weber, *Pogg. Ann.*, **73**. 139, 1848. Basic magnesium phosphate is precipitated if the magnesia mixture be in large excess, and magnesium sulphate is used in place of magnesium chloride for compounding the magnesia mixture (page 597).

[4] H. Struve, *Zeit. anal. Chem.*, **36**. 289, 1897; **37**. 485, 1898; K. K. Järvinen, *ib.*, **43**. 279, 1904; **44**. 333, 1905; R. Fresenius, H. Naubauer, and E. Luck, *ib.*, **10**. 133, 1870; C. Schumann, *ib.*, **11**. 382, 1872; H. Schmidt, *ib.*, **45**. 512, 1906; H. Neubauer, *Zeit. angew. Chem.*, **9**. 435, 1896; F. Raschig, *ib.*, **18**. 374, 1905; F. A. Gooch and M. Austin, *Amer. Journ. Science* (4), **7**. 187, 1899; W. Gibbs, *ib.* (3), **5**. 114, 1873; *Chem. News*, **28**. 51, 1873; R. W. C. MacIvor, *ib.*, **28**. 69, 1873; T. R. Ogilvie, *ib.*, **21**. 205, 1870; F. A. Gooch, *Amer. Chem. Journ.*, **1**., 391, 1879; A. K. Christomanos, *Zeit. anorg. Chem.*, **41**. 305, 1904; T. S. Gladding, *Journ. Amer. Chem. Soc.*, **4**. 135, 1882; *Chem. News*, **46**. 213, 1882; E. Raffa, *Gas. Chim. Ital.*, **38**. ii., 556, 1908.

[5] J. J. Berzelius (*Lehrbuch der Chemie*, Dresden, **2**. 650, 1826) used disodium phosphate. C. Mohr prefers sodium ammonium phosphate—microcosmic salt (*Zeit. anal. Chem.*, **12**. 36, 1873; W. Gibbs, *l.c.*)—because it precipitates more rapidly and completely. By precipitating more and more dilute solutions of magnesia, he arrived at a point where sodium phosphate no longer gave a precipitate under conditions where sodium ammonium phosphate did. L. Blum (*Zeit. anal. Chem.*, **28**. 452, 1889; W. Heintz, *ib.*, **9**. 16, 1867) prefers sodium phosphate, because the precipitate settles more rapidly than when sodium ammonium phosphate is the precipitating agent.

[6] In order to get rid of the ammonium salts which have accumulated in the solution which, it will be remembered, has been treated for both alumina and lime, some prefer to evaporate the filtrate nearly to dryness in a large dish. Add concentrated nitric acid; evaporate the solution to dryness, and heat the residue until all the ammonium salts have volatilised. Dissolve the mass in water, filter off any insoluble matter, and treat the solution as described in the text. The insoluble residue may be examined for alumina. This, if present, is precipitated, washed, and weighed as "extra alumina." J. Jámbor, *Zeit. anal. Chem.*, **49**. 733, 1910. See page 224.

Second Precipitation.—Redissolve the precipitate in warm dilute nitric acid (1 : 5), and collect the washings in the beaker in which the first precipitation was made. About 50 c.c. of acid are needed. While the acid is running through the funnel, turn the beaker round so that the acid runs all round the sides of the beaker. Add an aqueous solution containing a little sodium ammonium phosphate, and then add ammonia gradually with constant stirring, as in the first precipitation; wash as before; reject the filtrate and washings.

Ignition of the Precipitate.[5]—The precipitate may be collected on a Gooch's asbestos[6] crucible prepared in the usual manner. After the crucible has been dried and heated slowly over a Bunsen burner (in a Gooch's crucible saucer, page 106), it is heated over the Teclu's or Méker's burner for about 10 minutes. Cool in a desiccator and weigh. Ignite 4 or 5 minutes, cool, and weigh again. Repeat the ignition, if necessary, until the weight is constant.

If the precipitate be collected on a 7-cm. filter paper, the moist paper is placed in the crucible, dried and carbonised very slowly in the (platinum or porcelain) crucible,[7] placed obliquely on a triangle over, say, an argand burner, fig. 112. The temperature is gradually raised to redness, and there maintained until the precipitate appears white.[1] Finish the ignition over a weak blast. It is a bad practice to remove the last trace of carbon by blasting. The precipitate should be white before the blast is applied. If the contents of the crucible have a dirty white appearance, Fresenius[2] recommends moistening the precipitate with a few drops of nitric acid. Dry, and ignite as before. There is always a slight loss after the nitric acid treatment,[3] probably owing to the fact

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[1] This point requires careful attention. The precipitate will be more contaminated with impurities if quickly made. In illustration, a mean of six experiments in which the solutions were mixed suddenly gave 0·2028 grm. of $Mg_2P_2O_7$; another six experiments with the ammonia gradually mixed with constant stirring gave 0·1972 grm. $Mg_2P_2O_7$. Theory required 0·1971 grm. $Mg_2P_2O_7$. The stirring rod should be kept from the sides and bottom of the beaker. See H. Lasne, *Bull. Soc. Chim.* (3), 17. 823, 1897; *Chem. News*, 76. 270, 1897.

[2] Some keep the beaker under a bell jar resting on a greased ground-glass plate in order to prevent the evaporation of ammonia.

[3] Precipitates which take a long time to separate on standing frequently come down quickly if the solution be vigorously agitated—by, say, bubbling a current of air through the solution, or mechanical agitation—L. Briant, *Chem. News*, 53. 99, 1886; O. Texter, *Journ. Anal. App. Chem.*, 7. 279, 1893; V. Markoonikoff, *Liebig's Ann.*, 289. 254, 1895; H. B. Yardley, *New Remedies*, 9. 333, 1880.

[4] There is no particular need to here clean the precipitate from the sides and bottom of the beaker.

[5] K. Brookman (*Zeit. anal. Chem.*, 21. 551, 1882) dissolves the precipitate in nitric acid, and evaporates the solution to dryness in a weighed dish, ignites, etc. The object is to avoid loss by (1) the sticking of the precipitate to the walls of the beaker; (2) the "crawling" of the finely divided precipitate above the edge of the filter paper on to the funnel during washing; (3) as "dust" during the transfer of the dry filter paper to the crucible; and (4) loss as "dust" during the collapse of the ash of the filter paper during the ignition in the crucible. L. L. de Koninck (*Zeit. angew. Chem.*, 2. 187, 1888; *Zeit. anal. Chem.*, 29. 165, 1890; R. Fresenius, *ib.*, 15. 224, 1876; 16. 63, 1897) recommends a similar procedure for precipitates liable to reduction from the combustion of the filter paper, *e.g.*, ammonium and potassium chloroplatinates, ammonium magnesium arsenates and phosphates; cadmium and zinc carbonates, etc.

[6] H. N. Warren (*Chem. News*, 61. 63, 1890) recommends a plug of gun-cotton (pyroxylin) in place of asbestos. This burns away on ignition.

[7] It is not generally advisable to rest the triangle on the chimney of the argand burner, because the draught may be choked. The crucible is best supported on a triangle as shown in the diagram. If the precipitate be large, it should be dried and separated from the filter paper, so that the filter paper can be ignited alone. If a platinum crucible be employed for the ignition of the phosphate, and reducing agents (like carbon from the filter paper, reducing gases, hydrogen liberated from the decomposition of ammonia at high temperatures, etc.) be present, phosphides may be formed. These attack the platinum (W. C. Heraeus, *Zeit. angew. Chem.*, 15. 917, 1902; *Chem. News*, 97. 102, 1903; W. P. Headden, *Proc. Colorado Scientific Soc.*, 8. 45, 1905). Under ordinary conditions, however, there is little danger of this occurrence

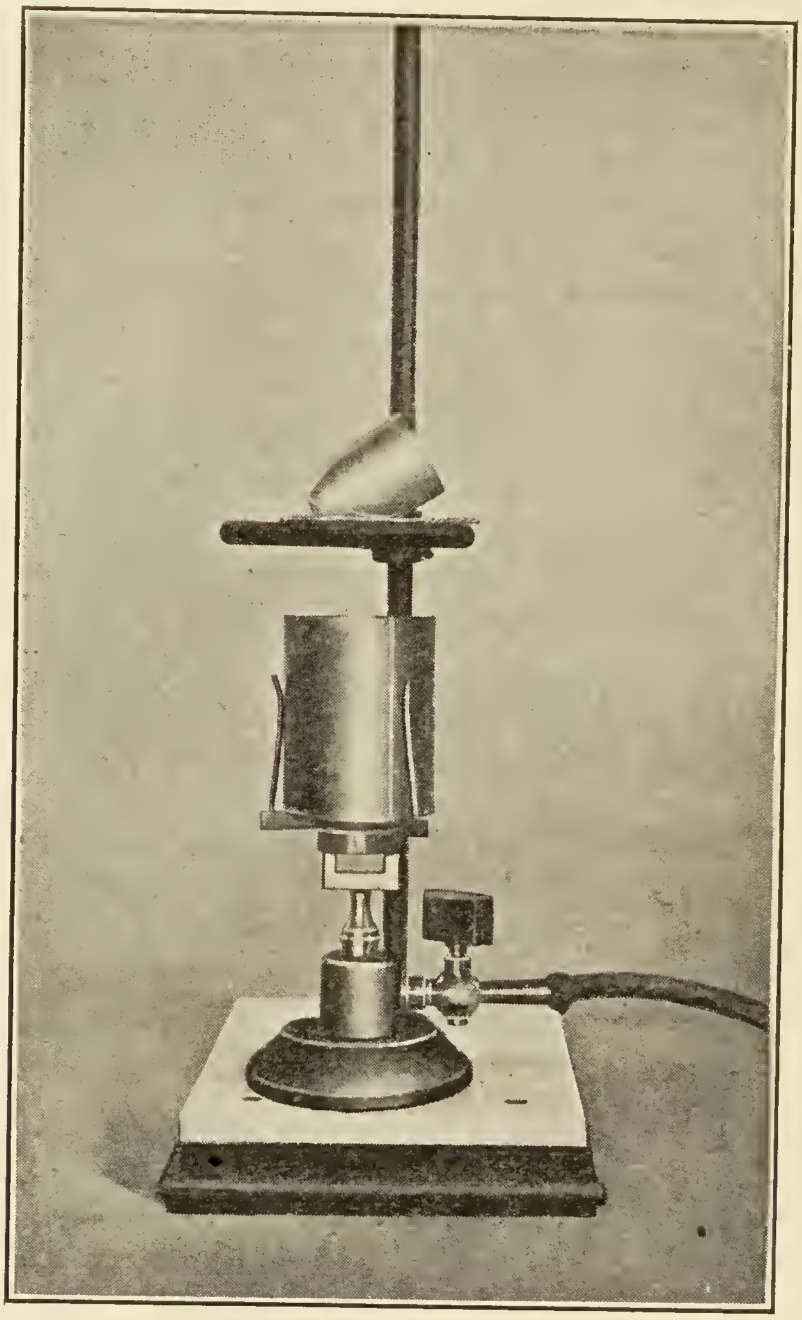

FIG. 112.—Ignition over Argand burner.

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during the ignition of the magnesium phosphates if the temperature of the blast be not high enough to fuse the pyrophosphate. The action, however, may easily occur if Gooch's platinum crucibles containing old precipitates be employed. The action is most marked if the ignition be conducted quickly in covered crucibles.

[1] When the precipitate is ignited too rapidly, there is a rapid shrinking and sintering. Particles of carbon are liable to be enclosed with the precipitate. It is then almost impossible to burn off the carbon by ignition, even in a blast (R. Bunsen ; F. Muck, *Zeit. anal. Chem.*, **19**. 131, 1880). L. L. de Koninck (*ib.*, **29**. 165, 1890) considers the frequent blackening of magnesium pyrophosphate is not due to particles of carbon derived from the filter paper, but to the presence of organic bases (*e.g.* pyridine) in commercial ammonia and its salts.

[2] R. Fresenius, *Quantitative Chemical Analysis*, London, **2**. 190, 1876.

[3] According to D. Campbell (*Chem. News*, **6**. 206, 1862), the treatment of magnesium pyrophosphate with nitric acid is objectionable, because the liberated phosphoric acid may volatilise at the high temperatures required for expelling the last traces of the nitric acid. J. O. Handy, *Journ. Amer. Chem. Soc.*, **22**. 31, 1900 ; E. Luck, *Zeit. anal. Chem.*, **13**. 255, 1874.

that some $H_4Mg(PO_4)_2$ is formed. This on ignition forms magnesium metaphosphate—$Mg(PO_3)_2$—which decomposes as indicated on page 216. After ignition to constant weight, cool in a desiccator, and weigh as $Mg_2P_2O_7$. This weight multiplied by 0·3620[1] gives the equivalent weight of MgO.[2] Instead of multiplying, the result may be read at once from Table XC.

Corrections.—Magnesia determinations are usually a little high owing to the presence of some impurities—lime, manganese, silica, etc.

(*a*) *Lime.*—There is not usually sufficient magnesia present in clays to render it advisable to apply Hillebrand's correction for lime.[3] If, however, over, say, 2 per cent. of magnesia be present, the correction may be made if the work is intended to be exact. Digest the pyrophosphate in a little dilute sulphuric acid, and add 9 to 9½ times its volume of absolute alcohol. After standing overnight, filter off the scarcely visible precipitate of calcium sulphate, and wash it free from phosphates by means of alcohol. Dry the precipitate; dissolve in hot water slightly acidulated with hydrochloric acid, and precipitate the lime in ammoniacal solution by means of ammonium oxalate (page 213). Filter, wash, ignite, and weigh as CaO. Add the result to the lime, and subtract it from the magnesium pyrophosphate.

(*b*) *Manganese.*—If this element[4] be present, it can be determined colorimetrically in the nitric acid solution of the precipitate. If present in the filtrate from the magnesia, evaporate to dryness; drive off the ammoniacal salts by ignition; and again evaporate the residue to dryness two or three times with nitric acid (or once with sulphuric acid) to drive off the chlorine. Determine the manganese colorimetrically, as indicated on page 382; and make the necessary allowance.

(*c*) *Silica.*—If silica be present, the magnesium pyrophosphate will leave a residue[5] when treated with the dilute sulphuric acid. This is filtered off, ignited, and weighed as indicated on page 185. The amount of silica is subtracted from the magnesium pyrophosphate.

(*d*) *Barium.*—See page 517 for barium in silica.[6]

Errors.—Some idea of the results may be gathered from the eight independent determinations on one sample of clay:—

0·0106; 0·0114; 0·0109; 0·0110; 0·0107; 0·0103; 0·0117; 0·0118;

with a mean of 0·0110 grm. MgO, representing 1·10 per cent. of MgO. The deviations from this value range between ± 0·08.

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[1] Or by 0·6378 for the equivalent weight of P_2O_5—page 597.

[2] M. Schmorger, *Zeit. anal. Chem.*, 37. 308, 1895; H. Mastbaum, *ib.*, 37. 581, 1898.

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 422. 127, 1910.

[4] The magnesium pyrophosphate has generally a pink colour if appreciable amounts of manganese be present.

[5] Some platinum sulphide may also be present (see page 186).

[6] B. Tollens (*Journ. Landw.*, 30. 48, 1883) says that if basic lime or magnesia phosphates are precipitated with the ammonium magnesium phosphate, and a little silver nitrate be added, a yellow colour will be developed when the precipitate is warmed.

CHAPTER XVII.

THE DETERMINATION OF THE ALKALIES.

§ 102. Meretricious Methods for Estimating the Alkalies.

1. *Difference Method.*—We shall see very shortly that the sum of the different constituents in a clay analysis may vary between 99·5 and 100·5. Assuming that the tolerated errors in the determination of the different constituents correspond with a total lying within 99·5 and 100·5, it follows that if the alkalies be determined by summing the different constituents actually determined, and subtracting the result from 100, the alkalies may be 0·5 per cent. greater or less than the number obtained by the process of subtraction. This means that a clay with 1 per cent. of alkalies might be reported with ½ or 1½ per cent., and the numbers mean that the clay might have anything between 0·5 and 1·5 per cent., on the assumption that the analysis has been conducted accurately. The number representing the alkalies would therefore be quite misleading unless interpreted as I have just indicated. It would certainly be better and more honest to report, "Alkalies not determined." It will also be noticed that when a constituent—say the alkalies—is determined by difference, and the whole analysis totals 100, there is no check on the accuracy of the analysis, and the numbers are accordingly under more or less suspicion.

2. *Calculation from the Supposed Quantities of Potash and Soda.*—There is another unsatisfactory method employed for estimating the alkalies.[1] The mixed chlorides are isolated and weighed. It is then assumed that the potassium and sodium chlorides are present in equal or some other proportions. The corresponding potash and soda are then calculated by arithmetic and reported as "alkalies." This method is possibly less objectionable than the preceding one, but it too must be condemned. It pretends to represent by number a magnitude which has not really been determined.[2] There is no method known for determining alkalies without separating them into "potash and soda."

§ 103. The Separation of the Alkalies as Mixed Chlorides—Smith's Process.

The alkalies in silicates are usually determined by first decomposing the clay by hydrofluoric acid, or by fusion with bismuth, lead, or boric oxides, etc.[3] The constituents other than alkalies are then removed. The mixed alkali salts remain behind as a residue.[4] One of the two following methods is generally employed. The most important, and one of the best for general work, is that devised by J. Lawrence Smith.[1] The following are the directions:—

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[1] At present rather too common.

[2] In illustration of both these vicious methods, see the two clay analyses, *Brit. Clayworker*, **19**. 155, 1910.

[3] E. Mäkinen (*Zeit. anorg. Chem.*, **74**. 74, 1912) fuses the silicate with calcium chloride, and otherwise proceeds as described in the text.

[4] E. Boujean, *Chem. News*, **80**. 240, 1899; A. Verweij, *Zeit. anal. Chem.*, **48**. 760, 1909; E. W. Dorfurt, *ib.*, **51**. 755, 1912.

The Crucible and Furnace.—An ordinary covered platinum crucible may be employed, but great care is then necessary not to heat the crucible at too high a temperature, nor should the crucible be heated to redness more than three-fifths of its height. The crucible recommended by Smith is best. It is a platinum crucible about 8 cm. long, 1·8 cm. wide at the mouth, and 1·5 cm. wide at the bottom. This crucible is placed at an angle of about 45° through the side of a fireclay cylinder, and heated to the full temperature of a Bunsen's burner as described below. Wrap a thin strip of asbestos paper round the crucible. This strip comes between the crucible and the fireclay jacket. It prevents the crucible jamming tightly in the aperture of the fireclay cylinder. The disposition of the fireclay cylinder and crucible is indicated in fig. 113. The source of heat is an ordinary Bunsen's burner with a flat-flame nozzle (fig. 113).

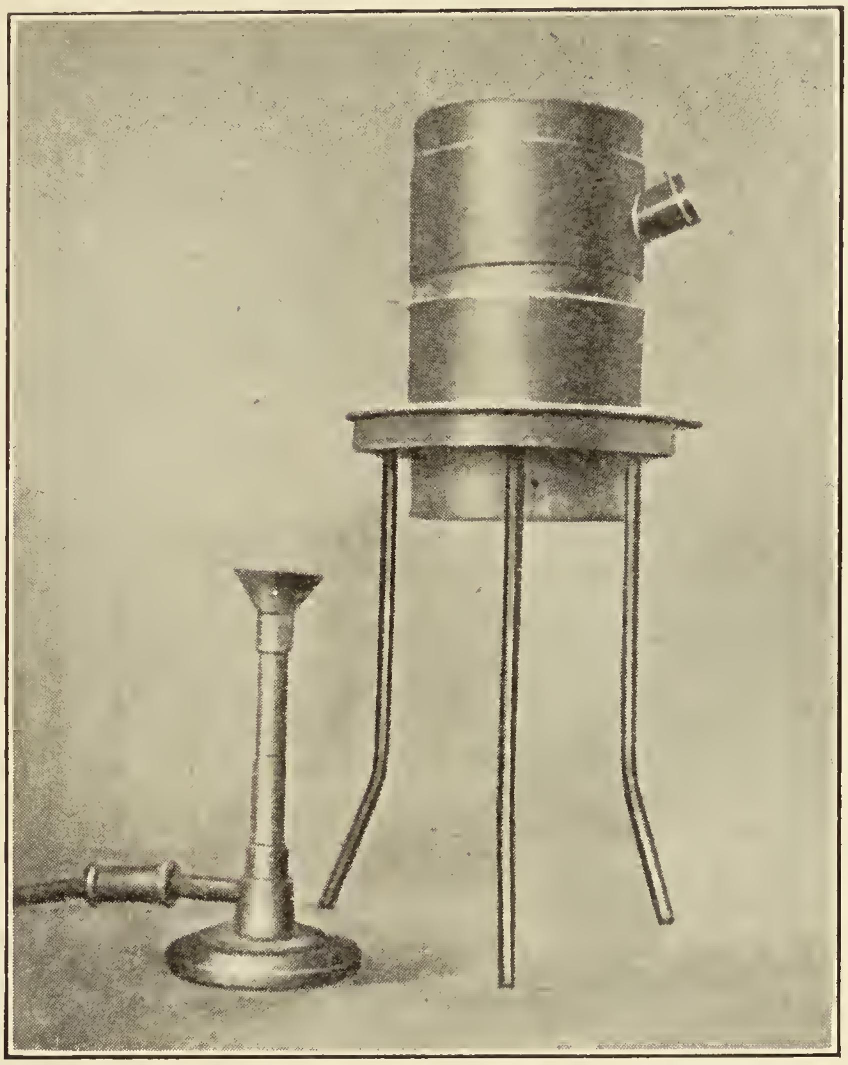

FIG. 113.—Furnace for L. Smith's process.

Preparation of the Sample for the Decomposition.—Spread about half a gram of calcium carbonate [2] as a layer on the bottom of the crucible. Intimately mix half a gram of ammonium chloride[1] with half a gram of the finely powdered and dried clay, and 3 grms.[2] of calcium carbonate. Transfer the mixture from glazed paper into the platinum crucible. Rinse the mortar and pestle and paper with another gram of calcium carbonate, and transfer the rinsings to the crucible.

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[1] J. L. Smith, *Amer. J. Science* (2), **50**. 269, 1871; *Chem. News*, **23**. 222, 234, 1871; P. Holland, *ib.*, **54**. 242, 1886; F. Field, *ib.*, **1**. 193, 217, 1860; T. Döring, *Zeit. anal. Chem.*, **49**. 158, 1910. R. L. Steinlen (*Chem. Ztg.*, **29**. 264, 1905; B. M. Margosches, *ib.*, **29**. 385, 1905) has devised a special cooler for the lid of the crucible, to prevent loss of alkalies by volatilisation.

[2] CALCIUM CARBONATE.—This is best made by dissolving calcite in hydrochloric acid. Heat the solution of calcium chloride to boiling, and add a hot concentrated solution of ammonium carbonate. Wash the precipitate thoroughly with hot water on a Büchner's funnel (page 103), and dry. This procedure gives a dense, coarse granular powder very suitable for this work. The calcium carbonate is generally contaminated with sodium chloride, but free from potassium chloride. This circumstance, and the fact that alkalies may be dissolved by the action of hot water on the glass vessels used in the analysis, render it necessary to find what correction must be made for the alkalies derived from the reagents, glass vessels, etc. This is done by treating the ½ grm. of ammonium chloride, and the 4½ grms. of calcium carbonate without the clay,

Ignition.—Heat the crucible, inclined as indicated above, very gently over a small flame for about 15 minutes, in order to volatilise the ammonium chloride. Then raise the temperature until the lower three-fifths of the crucible is at a dull red heat, and maintain this temperature for about an hour. Let the crucible cool. Beginners generally err by heating the crucible at too high[3] a temperature, when the mass vitrifies and then disintegrates with difficulty when treated with water.

Dissolution of the Cake in the Crucible.—Remove the cake from the crucible by adding 2 to 3 c.c. of water. After five or ten minutes, add more water. The sintered cake, not fused, usually comes away from the crucible quite readily. Transfer the contents of the crucible to a large porcelain or platinum dish. Heat the mass for about half an hour on the water bath with about 50 c.c. of water,[4] and restore that lost by evaporation from time to time. Triturate any large particles to powder with a small pestle. Decant the clear liquid through a filter paper. Wash about four times by decantation, and transfer the residue to the filter paper. Wash until the washings only give a faint turbidity with silver nitrate.[5] If the clay has been perfectly decomposed, the residue on the filter paper should leave no undecomposed residue when treated with hydrochloric acid.[6]

Removal of Lime.—Add ammonia and ammonium carbonate to the filtrate. Heat to boiling; filter; and again digest the precipitate with ammonia and ammonium carbonate. Filter, and allow the filtrate to collect with that from the previous filtration. Evaporate[7] the filtrate to dryness in a platinum or porcelain dish. Remove the ammonium salts by gentle ignition in a moving flame.[8] Treat the cold mass with water.[9] Remove the last traces of lime by the

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exactly as if the clay were present. A blank test made in this way gave 0·00022 grm. Na_2O and no K_2O for the materials quoted in the text. See M. Gräger, *Neues Jahrb. Pharm.*, **29**. 158, 1868. For barium carbonate in place of calcium carbonate and ammonium chloride, see G. Werther, *Journ. prakt. Chem.* (1), **91**. 321, 1864.

[1] AMMONIUM CHLORIDE.—The ammonium chloride is made by neutralising pure ammonia with pure hydrochloric acid, or by resubliming commercially pure ammonium chloride. J S. Stas, *Œuvres Complètes*, Bruxelles, **1**. 468, 1894; *Chem. News*, **15**. 194, 217, 231, 1867.

[2] If the silicate contains much iron, or is liable to sinter with the lime, increase the amount of calcium carbonate.

[3] A. Verweij (*Zeit. anal. Chem.*, 48. 760, 1909) uses a platinum crucible 4·5 cm. high and 3·5 cm. in width. He covers the mixture with a layer of 3 grms. of calcium carbonate, and after the expulsion of ammonia, heats the mixture for an hour over a Teclu's or powerful Bunsen's burner. The cold mass is boiled 15 minutes with water, etc.

[4] According to T. Döring (*Zeit. anal. Chem.*, **49**. 158, 1910), at least 500 c.c. of filtrate should be obtained per gram of sample, because the alkaline chlorides are retained tenaciously by the insoluble mass.

[5] The faint turbidity is possibly due to the presence of calcium oxychlorides which are slowly dissolved from the residue. Borates will be found in the insoluble residue.

[6] Some flecks of silicic acid may separate.

[7] G. H. Bailey (*Journ. Chem. Soc.*, **65**. 445, 1894) noticed a loss of alkaline chlorides during the evaporation of $\frac{1}{10}$N-solutions of alkaline chloride. For instance, lithium chloride lost 0·25 mgrm. per litre; sodium chloride, 0·81 mgrm. per litre; potassium chloride, 1·22 mgrms.; rubidium chloride, 2·95 mgrms.; and cæsium chloride, 3·35 mgrms. per litre.

[8] In specially exact work, the removal of the ammonium salts is best effected by heating the dish placed high above the flame (fig. 100). This requires about 45 minutes. If the ignition be conducted too rapidly, or the dish be too strongly heated, several milligrams of alkali may be lost; otherwise, A. Mitscherlich (*Journ. prakt. Chem.* (1), **83**. 459, 1861; J. Boussingault, *Compt. Rend.*, **64**. 1159, 1867) has shown that there is no loss of alkali during the expulsion of the ammonium salts. See page 218.

[9] If sulphur be present, add a drop of barium chloride solution, and remove the excess of barium by means of ammonium carbonate.

addition of ammonium oxalate to the boiling solution, and let the mixture stand overnight—about 12 hours.[1]

Determination of the Mixed Alkaline Chlorides.—Filter the liquid into a weighed platinum dish. Evaporate to dryness. Ignite. Cool. Moisten the residue with concentrated hydrochloric acid. Again evaporate to dryness. Ignite gently.[2] Weigh. The increase in weight represents the weight of the mixed—sodium and potassium—chlorides.[3]

The Accuracy of the Results.—The following numbers represent the results obtained with eight independent determinations on half-gram samples of the same clay:—

0·0226; 0·0229; 0·0233; 0·0229; 0·0228; 0·0221; 0·0225; 0·0222.

The mean value is 0·0227 grm. per half gram of clay; the deviations range approximately ± 0·0006 per grm. of clay. There is also a constant error due to the loss of alkali. L. Smith says: "Usually an amount of alkali remains behind amounting to 0·2 to 1·0 per cent. of the materials used." Smith recovers this by reheating the residue after the first sintering with the ammonium chloride mixture, and mixing the aqueous extract with the extract of the sintered mass obtained during the first heating. By proceeding as described above, the errors from this source will rarely exceed 0·002 grm. Holland has investigated the magnitude of the loss due to the retention of alkalies by the precipitate during the first extraction. He obtained:—

Table XXXIX.—Loss of Alkalies in Smith's Process.

Nature of silicate.	Mixed chlorides, in grms.	
	One fusion.	Re-fusion of residue.
Basalt (Wales)	0·1305	0·0040
Basalt (Westmoreland)	0·1118	0·0032
Leucite (Rieden, Germany)	0·2472	0·0034
Red spongy lava (Pompeii)	0·1434	0·0038
Syenite (North Wales)	0·1634	0·0029

Hence it is very probable that practically all but about 2 per cent. of the total alkali is extracted during the first operation. Under these conditions, about 2 per cent. of the total alkali is lost. This agrees with Dittrich's observation cited Table XLIII., page 247, and the result may be taken to represent the constant incidental to the process. The other chief errors arise from (1) too high a temperature for the fusion; (2) imperfect leaching of the fused mass; (3) driving off the ammonium chloride too rapidly; (4) spitting by too rapidly heating to drive off the ammonium salts; (5) igniting the mixed chlorides at too high a temperature; (6) imperfect separation of magnesium and calcium salts; and (7) the presence of sulphates. If the silicate contained appreciable quantities of sulphur, this element will be found as alkali sulphates along with the chlorides. The sulphates can be converted into chlorides by adding a little barium chloride before the final precipitation of the calcium is made. The excess of barium is removed by the ammonium carbonate and oxalate treatments.

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[1] Schaffgotsch's or Gooch and Eddy's solutions can also be used for the removal of lime and magnesia, as described in the next section.

[2] A. Mitscherlich (*Journ. prakt. Chem.* (1), **83**. 485, 1861) has shown that a six minutes' heating to the melting point of potassium chloride resulted in a loss of 0·0040 per cent., and 0·0042 per cent. of sodium chloride—H. Rose, *Pogg. Ann.*, **31**. 133, 1833; G. H. Mulder, *Archiv Pharm.* (2), **129**. 231, 1867; Reichmann, *Journ. Gasbeleuchtung*, **7**. 9, 1864; P. M. Delacharlonny, *Compt. Rend.*, **103**. 1128, 1886; H. B. von Adlerskron, *Zeit. anal. Chem.*, **12**. 390, 1873.

[3] If the residue dissolves in water, all is well. If not, filter off the insoluble matter, ignite and weigh. Deduct the weight of the insoluble residue from the weight of the total chlorides.

§ 104. The Separation of the Alkalies as Mixed Chlorides—Berzelius' Process.

It is sometimes convenient to decompose the silicate by a mixture of sulphuric and hydrofluoric acids, as recommended by Berzelius.[1] The alumina, lime, magnesia, etc., may be precipitated by mercuric oxide,[2] barium oxide,[3] or ammonium carbonate.[4] The alkali salts remain in solution. The following plan gives good results. It is rather quicker than Smith's process, but more expensive materials are needed. The "yield" of mixed chlorides is also about 1 per cent. (on the "total alkali") higher than in Smith's process. Berzelius' process is not recommended when the silicate contains boron compounds. In Smith's process the boron remains behind as insoluble calcium borate.

Removal of Silica, Alumina, and Iron.—Mix 1 grm. of the clay in a platinum crucible with 50 c.c. of concentrated sulphuric acid, and add carefully, in small quantities at a time, about 50 c.c. of hydrofluoric acid.[5] Heat gently on a sand bath; when the hydrofluoric acid has evaporated, add another 50 c.c. of hydrofluoric acid, and heat as before. When the hydrofluoric acid has nearly gone, evaporate the solution to dryness. Cool. Add concentrated aqueous ammonia, and heat gently. When the mass is quite disintegrated, filter and wash with hot water.

Transformation of the Sulphates into Chlorides.—It is now advisable to transform the sulphates in the filtrate into chlorides[6] by precipitating the sulphates as barium sulphate, and removing the excess of barium chloride as barium carbonate[1] in the following manner :—Acidify the filtrate with hydrochloric acid,[2] and heat the solution to boiling. Add an excess of a hot solution of barium chloride[3] to the boiling solution. Heat the mixture to boiling, and let it stand overnight. Filter; wash with hot water; evaporate the filtrate to dryness in a platinum dish; ignite to drive off the ammonium salts; and cool. The barium is removed during the next operation.

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[1] J. J. Berzelius, *Pogg. Ann.*, **1**. 169, 1824; E. A. Wülfing, *Ber.*, **32**. 2214, 1899; C. Reinhardt, *Stahl Eisen*, **16**. 448, 1896; W. Knopp, *Zeit. anal. Chem.*, **22**. 421, 558, 1883; **18**. 462, 1879; *Chem. News*, **48**. 110, 1883; A. H. Low, *ib.*, **67**. 185, 1893; *Journ. Anal. App. Chem.*, **6**. 666, 1892.

[2] E. F. Smith and P. Heyl, *Zeit. anorg. Chem.*, **7**. 82, 1894; *Chem. News*, **70**. 193, 204, 1894; G. Starck, *Zeit. anal. Chem.*, **48**. 415, 1909.

[3] J. N. von Fuchs, *Schweigger's Journ.*, **62**. 184, 1831; H. Rose, *Pogg. Ann.*, **83**. 137, 1851; C. Zimmermann; J. E. Thomsen, *Journ. Amer. Chem. Soc.*, **30**. 420, 1908.

[4] F. G. Schaffgotsch, *Pogg. Ann.*, **104**. 482, 1858; H. Weber, *Vierteljahr. prakt. Pharm.*, **8**. 161, 1859. Schaffgotsch's solution is made by dissolving 230 grms. of ammonium carbonate in 180 c.c. of aqueous ammonia (sp. gr. 0·92) and making the solution up to a litre. F. A. Gooch and E. A. Eddy, *Chem. News*, **97**. 280, 1908; *Amer. J. Science* (4), **25**. 444, 1908; F. A. Gooch and M. A. Phelps, *ib.* (4), **22**. 488, 1906; F. A. Gooch, *ib.* (3), **48**. 216, 1893; P. E. Browning and W. A. Drushel, *Zeit. anorg. Chem.*, **54**. 151, 1907; E. Divers, *Journ. Chem. Soc.*, **61**. 196, 1892; E. Bonjean, *Bull. Soc. Chim.* (3), 21, 1899; *Chem. News*, **80**. 248, 1899.

[5] R. Kayser (*Zeit. öffent. Chem.*, **5**. 107, 1900) found 2·4 per cent. of potash in one sample, and 1·4 per cent. of potash and 0·6 per cent. soda in another sample of so-called "chemische reine Flusssäure." Hence the necessity for testing this acid for alkalies. See pages 163 and 446.

[6] According to H. Rose (*Pogg. Ann.*, **74**. 568, 1848), when alkaline sulphates are mixed with ammonium chloride and exposed to a red heat, the alkaline sulphate is partly, and on repeated application of the process wholly, transformed into the chloride. E. Nicholson (*Chem. News*, **26**. 147, 1872) claims that this reaction is of no use as an analytical process. According to F. C. Phillips (*Zeit. anal. Chem.*, **13**. 149, 1874; M. Chikashigé, *Chem. News*, **71**. 17, 1895), for complete conversion, the temperature of ignition should be just short of the melting point of sodium and potassium chlorides, and the best way of converting the sulphates to chlorides is to evaporate the solution to dryness in a platinum basin with ammonium chloride. Mix the residue with dry powdered ammonium chloride and calcine to a constant weight in a covered crucible to avoid loss by volatilisation.

Removal of Magnesia and Lime.—The main difficulty in this process is the removal of the magnesia. The ammonium magnesium carbonate is appreciably soluble in ammoniacal ammonium carbonate (Schaffgotsch's solution), and an exact separation is not possible by this reagent. Gooch and Eddy have shown that an alcoholic "Schaffgotsch's" solution is quite effective, since the precipitation of the magnesia is then complete. Evaporate the solution to about 50 c.c.; add 50 c.c. of absolute alcohol, and 50 c.c. of an alcoholic solution of ammonium carbonate—Gooch and Eddy's solution.[4] Stir the mixture thoroughly, and let it stand about 20 minutes. Filter, and wash with Gooch and Eddy's reagent. Dissolve the precipitate in dilute hydrochloric acid, add an excess of ammonia, and repeat the treatment. Collect the filtrate in a weighed platinum dish, and evaporate the liquid to dryness. Drive off the ammonium carbonate by gentle heating. Add a drop of hydrochloric acid. Ignite, cool, and weigh the mixed chlorides.

§ 105. The Indirect Determination of Potash and Soda.

In some cases it is possible to determine, quite accurately, the potash and soda in the mixed chlorides[5] by the so-called "indirect process." The weight of the mixed chlorides is first determined, and afterwards the total chlorine by, say, Mohr's process (page 79). From the data so obtained, it is possible to deduce the respective amounts of soda and potash by arithmetic.

Let KCl denote the weight of potassium chloride and NaCl the weight of sodium chloride in the mixture. Let w denote the weight of the mixed chlorides, and u the weight of chlorine in the mixture. Then, obviously, the weight of the mixed chlorides is

$$\mathrm{KCl} + \mathrm{NaCl} = w \quad . \quad . \quad . \quad . \quad . \quad (1)$$

One part by weight of sodium chloride contains 0·6047 part of chlorine, and one part by weight of potassium chloride contains 0·4756 part of chlorine. Hence, the total weight of chlorine may be written :

$$0{\cdot}6047\mathrm{NaCl} + 0{\cdot}4756\mathrm{KCl} = u \quad . \quad . \quad . \quad . \quad (2)$$

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[1] Better results are obtained at a later stage by working with chlorides, although some get the alkalies at the last stage as mixed sulphates instead of mixed chlorides, and determine the potassium as potassium chloroplatinate in the mixed sulphates. The small amount of sulphuric acid liberated during the double decomposition: $K_2SO_4 + H_2PtCl_6 = K_2PtCl_6 + H_2SO_4$, does not appreciably affect the results.

[2] There is a slight loss of alkaline chlorides by adsorption. The barium sulphate carries down less potassium salts when the precipitation is made in solutions but feebly acid—B. West, *Zeit. anal. Chem.*, **20**. 357, 1881. J. F. de Vries (*Chem. Weekblad*, **5**. 261, 1908) found 26·6 instead of 27·0 per cent. K_2O. The loss was due to the potassium salt retained by the barium sulphate.

[3] Commercial "guaranteed pure" barium chloride not infrequently contains potassium salts. Hence attention must be paid to this matter, otherwise high results may be obtained.

[4] GOOCH AND EDDY'S SOLUTION.—Mix 180 c.c. of ammonia, 800 c.c. of water, 900 c.c. as absolute alcohol, and saturate the mixture with ammonium carbonate. Filter off any insoluble salt.

[5] The method for the mixed sulphates is quite similar in principle.

These two relations suffice for the computation. Solve the first equation for NaCl, and substitute the result in the second. We thus obtain, on reduction,

$$KCl = 4{\cdot}609w - 7{\cdot}622u\,; \quad \text{and} \quad NaCl = w - KCl$$

by substituting the value of KCl so obtained, in the first equation. The conversion of the amounts of the two chlorides so obtained into the equivalent oxides is effected in the usual manner, namely:—

$$\text{Amount of } KCl \times 0{\cdot}6317 = \text{Amount of } K_2O\,;$$
$$\text{Amount of } NaCl \times 0{\cdot}5303 = \text{Amount of } Na_2O.$$

This method does not give good results with the small amounts of alkalies found in clays, unless very special care be taken to ensure the absence of magnesium and other metallic chlorides. Collier[1] obtained quite satisfactory results with mixtures of *pure* salts: for instance:—

Table XL.—Test Analyses—Indirect Separation of Potassium and Sodium Chlorides.

Mixed together.		Found.		Chlorine.	
KCl.	NaCl.	KCl.	NaCl.	Found.	Calculated.
0·0582	...	0·0573	0·0009	0·0278	0·0277
0·1284	0·0067	0·1284	0·0067	0·0651	0·0651
0·0967	0·0102	0·0967	0·0102	0·0522	0·0522
0·0782	0·0317	0·0783	0·0316	0·0564	0·0564
0·0305	0·0379	0·0304	0·0380	0·0375	0·0375
0·0101	0·1029	0·0104	0·1026	0·0672	0·0672
0·0065	0·1100	0·0058	0·1107	0·0699	0·0698
...	0·0590	...	0·0605	0·0360	0·0358

According to Virgili, the relative errors involved in the indirect processes for sodium and potassium salts are those indicated in Table XLI., on the assumption that pure salts are being treated.

Table XLI.—Relative Errors in Indirect Processes for the Determination of Soda and Potash.

Determination.	Mixture contains	Relative error.	
		Sodium salt.	Potassium salt.
Total chlorine in the mixed chlorides	NaCl : KCl	NaCl ±0·018	KCl ±0·014
	NaCl : 10KCl	NaCl ±0·102	KCl ±0·008
Conversion chlorides into sulphates	NaCl : KCl	NaCl ±0·021	KCl ±0·017
	NaCl : 10KCl	NaCl ±0·118	KCl ±0·010
Total SO_4 in the mixed sulphates	$Na_2SO_4 : K_2SO_4$	Na_2SO_4 ±0·021	K_2SO_4 ±0·017
	$Na_2SO_4 : 10K_2SO_4$	Na_2SO_4 ±0·118	K_2SO_4 ±0·010

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[1] P. Collier, *Amer. J. Science* (2), **37**. 344, 1865; *Chem. News*, **10**. 182, 1864; F. M. Lyte, *ib.*, **29**. 159, 1874; E. Fleischer, *ib.*, **19**. 265, 300, 1869; F. Mohr, *Lehrbuch der Titriermethode*, Braunschweig, 364, 1859; *Zeit. anal. Chem.*, **7**. 173, 1868; M. Kretschy, *ib.*, **15**. 37, 1876; H. Schiff, *Liebig's Ann.*, **105**. 219, 1858; T. Thomson, *ib.*, **20**. 205, 1836; K. List, *ib.*, **81**. 117, 1852; S. Panpushka, *Journ. Phys. Chem. Ges. St. Petersburg*, **19**. 106, 1888; *Zeit. anal. Chem.*, **27**. 160, 1888; L. W. Winkler, *Chem. Ztg.*, **24**. 816, 1900; G. Errera, *Gazz. Chim. Ital.*, **18**. 244, 1889; E. K. Landris, *Journ. Amer. Chem. Soc.*, **17**. 466, 1895; **18**. 132, 1896; G. Werther, *Journ. prakt. Chem.* (1), **91**. 324, 1864; J. J. Berzelius, *De l'Analyse des Corps Inorganiques*, Paris, 69, 1827; J. P. Wuite, *Chem. Weekblad*, **4**. 19, 1907. A. J. Sofianopoulos (*Bull. Soc. Chim.* (4), **5**. 632, 1909) converts the mixed chlorides into fluorides. The process has not been thoroughly tested in general work.

To illustrate the effect of impurities on the determination, suppose a mixture of potassium chloride, 0·200 grm., and sodium chloride, 0·020 grm., has 0·002 grm. of magnesium chloride as impurity, the calculated potassium and sodium chlorides (supposing that there are no analytical errors) will be respectively 0·190 grm. potassium chloride and 0·027 grm. sodium chloride, in place of 0·200 grm. and 0·020 grm. respectively. Suppose further that a similar mixture of potassium and sodium chlorides has 0·002 grm. of an inert impurity, say, 0·002 grm. of magnesia. Then, under the above conditions, 0·206 grm. of potassium chloride and 0·016 grm. of sodium chloride would be obtained, in place of 0·200 grm. and 0·020 grm. respectively.

This all means that *the indirect process will give exact results with large or small amounts of the mixed chlorides when no impurity is present.* Consequently, when there are no means of establishing the purity of the mixture, and *when the alkalies appear at the end of a long series of separations, the method will not be very reliable, since the method of calculation multiplies a small trace of impurity into a relatively large error.* Some consider that the errors by the indirect process are less than the experimental errors by the direct process (*e.g.*, List, Rose, etc.). This is probably the truth about the method with the limitations just stated.[1]

§ 106. A General Study of Indirect Separations.

This seems rather an attractive and speedy method of resolving the bases in a mixture, and the student might well inquire why the principle is not more extensively applied for determining, say, potash and soda; cobalt and nickel; lime and magnesia; lime and strontia; etc. It is therefore necessary to study the principle in more detail. The problem may be stated in general terms:—

Given a mixture of two salts with different bases and one acid, or with different acids and one base, to find the amount of each constituent.—Let the salts have the general formulæ MA and NA;[2] and further, let the total weight of the mixture be w, and the weight of the common constituent u. It is required to find the weights of M and N in the mixture. For convenience, let x denote the weight of M, and y the weight of N. Let a denote the known weight of A in the salt MA, and b the weight of A in the salt NA. Hence, it follows:

$$(x+a)+(y+b)=w\,; \quad \text{and,} \quad a+b=u.$$

Further, it follows from the laws of chemical combination that $a:x=A:M$, and $b:y=A:N$, where A, M, and N now denote the equivalent weights of the respective constituents represented by the letters. Then,

$$\frac{a}{x}=\frac{A}{M};\ \frac{b}{y}=\frac{A}{N}.$$

These four equations suffice for the algebraic solution of the four unknowns—x, y, a, and b—from the given data. Solving these equations in the usual manner, we get

$$\frac{A}{M}x+\frac{A}{N}y=u \qquad . \quad . \quad . \quad . \quad . \qquad (3)$$

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[1] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 441, 1863; H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**. 17, 1871. R. Bunsen (*Zeit. anal. Chem.*, **10**. 400, 1871) considers the indirect process a useful means of controlling the results by the direct process. J. Dennant (*Rep. Australasian Assoc.*, **2**. 385, 1890) objects.

[2] If A be bivalent, and M or N univalent, say, M_2A and N_2A, then we write $M'=2M$ in place of M; and conversely, if A be univalent, and N or M bivalent so that the salts are MA_2 and NA_2, we write $A'=2A$ in place of A. In the first case, M′, N′, and A are chemically equivalent, and in the second case M, N, and A′ are chemically equivalent.

which corresponds with equation (1) above. From the first pair of equations, we get

$$x + y = w - u \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Solving this equation for y, and substituting the result in the first equation, we get

$$x = \frac{M}{A} \cdot \frac{u(N+A) - wA}{N-M}; \text{ and } y = \frac{N}{A} \cdot \frac{u(M+A) - wA}{M-N} \quad . \quad . \quad (5)$$

The last equation is not needed in the actual arithmetic, because it is easier to calculate y from the value of x, w, and u in equation (4). These equations (5) generalise the method employed on page 227 in solving a particular problem.

Conditions for Success.—Let us interpret the equations further. It is easy to see that if $u(M+A) - wA = 0$, x must be zero, and

$$\frac{u}{w} = \frac{A}{N+A}.$$

This means that if, in the analysis of a mixture of, say, the alkaline chlorides, we get a relation such that

$$\frac{u}{w} = \frac{35{\cdot}5}{23 + 35{\cdot}5} = \frac{35{\cdot}5}{58{\cdot}5},$$

no potassium chloride is present.

If N be less than M in magnitude, we have $u(N+A)$ greater than wA, since, if wA were the greater, x would be negative, and negative values of x are impossible. Consequently, we have

$$\frac{u}{w} > \frac{A}{N+A}.$$

Every addition of KCl to NaCl makes the ratio $u : w$ greater than $A : N + A$; or greater than 35·5 : 58·5.

When $M = N$, as is nearly the case with a mixture of cobalt and nickel salts, the indirect analysis is impossible because $M - N$ will then be zero, and equations (5) cannot be solved.

By rearranging the first of equations (5), and expressing the percentage amount of x in a mixture weighing w grams, we have

$$\frac{100M}{A(N-M)} \left(\frac{u(N+A) - wA}{w} \right) \text{ per cent. of } M.$$

We see at a glance that the factor on the left is constant for a particular pair of salts, and that the greater the value of this factor, the greater the influence of errors in the determination of u and w on the final result. With a mixture of potassium and sodium chlorides, the factor is nearly 7; with magnesium and calcium sulphates, 9; and with nickel and cobalt sulphates, 555. It is thus easy to see, other things being equal, that a mixture of magnesium and calcium sulphates can be estimated nearly, but not quite, as accurately as a mixture of potassium and sodium chlorides, while the indirect separation of nickel and cobalt sulphates is hopeless, because the errors in the determination are multiplied enormously. Hence, other things being equal, the calculated values of x and y will be the more accurate—

(1) The smaller the numerical values of the equivalent weights of the constituents M and N;

(2) The greater the difference between the equivalent weights of the constituents M and N;

(3) The greater the equivalent weight of the single constituent A; and
(4) The nearer the ratio of the weights $u : w$ to the ratio of their equivalent weights $M : N$.[1]

§ 107. The Properties of Sodium and Potassium Chloroplatinates.

In place of the preceding process it is usual to determine the potassium chloride separately, and subtract this from the weight of the mixed chlorides. The remaining weight of sodium chloride is multiplied by 0·5303 to get the equivalent amount of sodium oxide. The process of separation depends upon the facts: (1) that a mixture of sodium and potassium chlorides in contact with a solution of hydrochloroplatinic acid—H_2PtCl_6—forms both sodium and potassium chloroplatinates;[2] and (2) there is a marked difference in the solubility of the two salts in alcoholic solution.

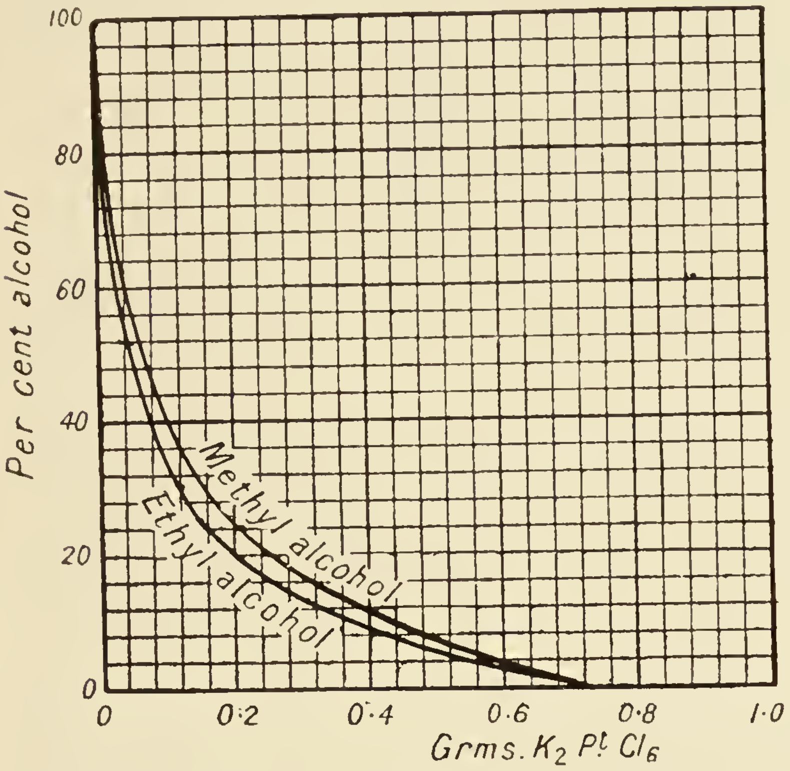

FIG. 114.—Potassium chloroplatinate (Archibald, Watson, and Buckley).

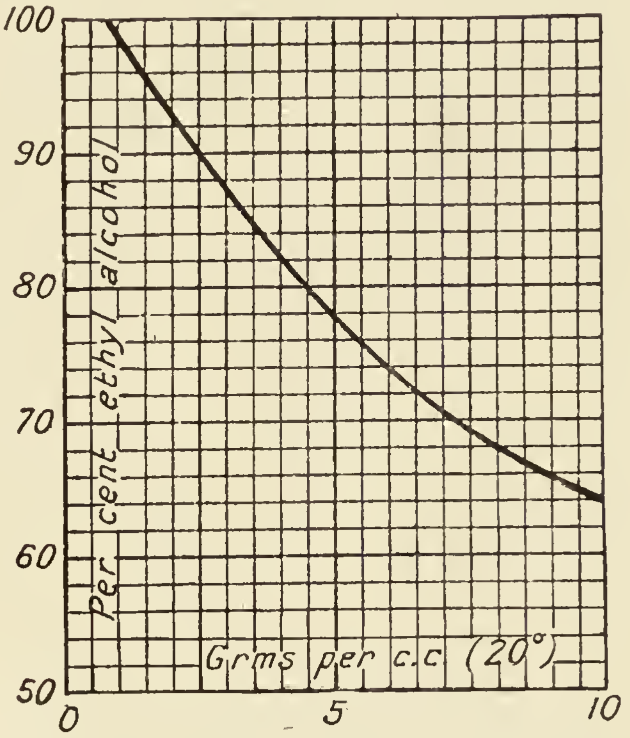

FIG. 115.—Sodium chloroplatinate (Péligot).

Solubilities of Sodium and Potassium Chloroplatinates in Alcoholic Solutions.—Both sodium and potassium chloroplatinates are appreciably soluble in water. The solubilities of sodium and potassium chloroplatinates in different proportions of ethyl and methyl alcohol and water are indicated by the graphs, figs. 114–115.[3] These results show that the greater the concentration of the alcohol, the less the solubility of the chloroplatinate, and that the potassium salt is less soluble in ethyl than in methyl alcohol.

Different investigators have different ideas as to the best strength of the alcoholic solution, and we find numbers ranging from 70 to 100 per cent alcohol[4] recommended for the washing, etc. If we were guided only by the solubility, we should recommend the use of absolute alcohol. But the Versuchstationen at Halle and Darmstadt[1] have shown that alcohol of greater concentration than 96 per cent. gives too high results.

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[1] When the errors in the determination of u and w are the same. For a more exact study of the relations between the calculated values of x and y and the experimental errors in the determination of u and w, see J. W. Mellor, *Higher Mathematics*, London, 539, 1909; and for a discussion on the indirect methods of analysis, see J. Fages y Virgili, *Die indirekten Methoden der analytischen Chemie*, Stuttgart, 1911.

[2] Also called platinichlorides, not platinochlorides.

[3] M. Péligot, *Monit. Scient.* (4), **6**. 872, 1892; H. Precht, *Chem. Ztg.*, **20**. 209, 1896; R. Bunsen and G. Kirchhoff, *Pogg. Ann.*, **113**. 337, 1861; E. H. Archibald, W. G. Watson, and B. G. Buckley, *Journ. Amer. Chem. Soc.*, **30**. 747, 1908.

[4] H. Precht (*Zeit. anal. Chem.*, **18**. 509, 1879; H. Precht, H. Vogel, and H. Haefcke, *Lands. Ver. Stat.*, **47**. 97, 1896) recommends absolute alcohol. R. Finkener (*Pogg. Ann.*, **29**.

Decomposition of Sodium Chloroplatinate by Concentrated Alcoholic Solutions.—Morozewicz[2] claims to have traced the high results with concentrated alcohol to the decomposition of part of the sodium chloroplatinate, by alcohol of greater concentration than 90 per cent., into sodium chloride[3] and soluble platinum chloride; and three or four times more of the hydrochloroplatinic acid is needed to convert all the sodium into sodium chloroplatinate. The presence of the insoluble cubic crystals of sodium chloride intermixed with the potassium chloroplatinate is supposed to explain the high results obtained when the alcohol employed for the washing, etc., is too concentrated. There is no danger of the formation of the sodium chloride with 80 per cent. alcohol, but another danger arises, owing to the solubility of the potassium chloroplatinate in the alcohol.[4] This means that 0·0001 grm. of potassium chloride, or 0·000064 grm. of potassium oxide, must be added to the final result for every 10 c.c. of 80 per cent. alcohol which comes in contact with the precipitate.[5] As a rule, less than 50 c.c. of the alcoholic solution are used in clay analyses, and in consequence the solubility correction may usually be neglected.[6]

Effect of the Concentration of the Solution on Precipitated Potassium Chloroplatinate.—We now inquire: should the hydrochloroplatinic acid be added to a concentrated or to a dilute solution of the two chlorides? Fresenius[7] recommends a concentrated solution. In this case, a fine pulverulent precipitate is formed, which appears under the microscope to be a mixture of stellate groups of

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637, 1866) and D. Lindo (*Chem. News*, **44**. 77, 86, 97, 129, 1881), 98 per cent. alcohol; the Stassfurter Kaliindustrie, 96 to 100 per cent.; B. Sjollema (*Chem. Ztg.*, **21**. 739, 1897), 90 per cent. alcohol; and A. Atterberg (*Zeit. anal. Chem.*, **36**. 314, 1897; *Chem. Ztg.*, **22**. 523, 538, 1898), 80 per cent. alcohol. H. Fresenius (*Chem. Ztg.*, **34**. 1032, 1910) states that 70 per cent. alcohol gives too low results, 85 per cent. too high; and 80 per cent. alcohol gives correct results.

[1] *Lands. Ver. Stat.*, **45**. 374, 1894; **46**. 181, 1895.

[2] J. Morozewicz, *Ber. Acad. Sciences Cracovie*, 796, 1906. F. P. Treadwell (*Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 38, 1911) does not think that the sodium chloroplatinate is decomposed in the manner stated by Morozewicz. W. A. Davis (*Chem. World*, **1**. 219, 1912) agrees with Morozewicz.

[3] F. Röttger and H. Precht (*Ber.*, **18**. 2076, 1885) show that, at 15°, 100 grms. of alcohol dissolve the following amounts of sodium and potassium chlorides:—

Alcohol	90	92·5	95	per cent.
Sodium chloride	0·345	0·223	0·146	grm.
Potassium chloride	0·073	0·043	0·028	grm.

[4] According to Péligot, the solubility of the potassium chloroplatinate is rather less in methyl alcohol (but see fig. 114), and, in consequence, some recommend the use of methyl alcohol in place of ordinary ethyl alcohol. P. Rohland (*Zeit. anorg. Chem.*, **15**. 412, 1897; **16**. 306, 1898; *Zeit. anal. Chem.*, **49**. 358, 1910) points out that methyl alcohol has additional advantages. If the precipitation be made in the presence of barium chloride, the barium chloroplatinate is liable to decompose into barium chloride and platinum chloride. The former is fairly soluble in methyl alcohol (78 parts of absolute methyl alcohol, at 15°, dissolve 1 part of barium chloride), and practically insoluble in ethyl alcohol even at 80 per cent. concentration. After washing in methyl alcohol Rohland finishes off by washing with ether. The potassium chloroplatinate is less soluble in a mixture of alcohol and ether than in alcohol alone, and R. Finkener (*l.c.*) recommends a mixture of absolute alcohol and ether in the proportions 2 : 1, while B. C. Corenwinder and G. Contamine (*Compt. Rend.*, **89**. 907, 1879) recommend a mixture of 95 per cent. alcohol with ether in the proportions 9 : 1; and H. N. Warren (*Chem. News*, **75**. 256, 1897) recommends a mixture of amyl alcohol and ether.

[5] The volume is easily measured if the filtration be conducted in a Gooch's crucible in a Witt's filtration jar (page 99), containing a measuring cylinder. The measurement, however, need be only approximate.

[6] H. Fresenius and P. H. M. P. Brinton, *Zeit. anal. Chem.*, **50**. 21, 1911.

[7] R. Fresenius, *Zeit. anal. Chem.*, **16**. 63, 1877; **21**. 234, 1882.

crystals with a few octahedral crystals. If the hydrochloroplatinic acid be added to a dilute solution, and subsequently evaporated down, the crystals are mainly octahedral. In both cases the crystals belong to the cubic system. Those formed in concentrated solution appear to be octahedra distorted into rod-like crystals. The crystals formed in concentrated solution also contain a relatively large number of cavities, which enclose minute globules of the mother liquid, while the octahedral crystals contain, as a rule, comparatively few inclusions. These facts are rather important. The crystals with the liquid inclusions must give high results, since the resulting precipitate contains potassium chloroplatinate plus mother liquid. The crystals can be more or less perfectly dried, but the result will then still be high, presumably owing to the residue left on evaporation of the liquid to dryness. Difficulties are also encountered in drying the potassium chloroplatinate formed in concentrated solutions. This is exemplified by the following experiment, due to Winton.[1] In one case, a mixture of 1·018 grms. of potassium chloride and 0·541 grm. of sodium chloride was made up to 100 c.c.; and in another case, a mixture of 13·063 grms. of potassium chloride and 0·541 grm. of sodium chloride was also made up to 100 c.c. Corresponding volumes were treated with hydrochloroplatinic acid. The resulting precipitates were treated in the same way, and their weights, after drying for the periods stated in Table XLII., and at the stated temperatures, were determined. The results are shown in Table XLII.

The Drying of Potassium Chloroplatinate.—Obviously, a more protracted drying at a relatively high temperature is needed to dehydrate crystals formed in a concentrated solution, than when the crystals are formed in a dilute solution. This result also explains how different investigators have made different recommendations at this stage of the analysis. Fresenius, for example, says that 30 hours at 130° are needed, while Eggertz and Nilson say that from 10 minutes to 4 hours suffice.[2]

Table XLII.—Effect of drying Potassium Chloroplatinate formed in Dilute and in Concentrated Solutions.

Temperature of oven. °C.	Hours drying.	Precipitated in dilute solution.	Precipitated in concentrated solution.
100	2	99·57	100·22
100	8	99·57	100·03
100	14	99·57	99·95
100	20	99·56	99·93
130	26	99·56	99·80
130	38	99·55	99·70
130	66	99·55	99·67
160	84	99·52	99·56
160	102	99·51	99·50

The "Atomic Weight" of the Platinum in Potassium Chloroplatinate.—The older analysts used the number 197 for the atomic weight of platinum, whereas recent work shows that the atomic weight of this element is nearer 195. The former number gives the factor 0·3056 for converting the weight of the potassium chloroplatinate into potassium chloride, while the later number gives the factor 0·30688. The "wrong" number apparently gives a result nearer the truth, unless certain modifications be made in the conduct of the analysis (page 250).

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[1] A. L. Winton, *Journ. Amer. Chem. Soc.*, **17**. 453, 1895; Ruer, *Chem. Ztg.*, **20**. 270, 1896; F. T. B. Dupré, *ib.*, **20**. 305, 1896.

[2] R. Fresenius, *l.c.*; C. G. Eggertz and L. F. Nilson, *Königl. Land. Akad. Hand. Tids.*, **35**. 326, 1898; G. Krause, *Archiv Pharm.* (3), **2**. 407, 1874.

The Transformation of Potassium Chloroplatinate into Metal before Weighing.—Owing to possible errors arising from the contamination[1] of the potassium chloroplatinate when precipitated in contact with barium chloride, as is necessary in some special cases, some reduce[2] the chloroplatinate to metal, wash out the soluble salts, and multiply the weight of the metal by the necessary factor to get the equivalent potassium chloride or oxide. The chlorine may also be determined in the soluble salts by titration according to Volhard's or Mohr's processes (pages 76 and 79), and the result calculated to potassium chloride or oxide.[3] These methods are not usually employed in silicate analyses.

§ 108. The Separation of Potassium as Potassium Chloroplatinate.

Precipitation of Potassium Chloroplatinate.—Treat a dilute solution of the mixed chlorides in a small porcelain basin with 0·3 c.c. more than the amount of hydrochloroplatinic acid calculated[4] on the assumption that the mixed chlorides are all sodium chloride. Evaporate the solution[1] to a syrupy consistency[2] on a water bath.[3] Cool. The mass should form a solid cake.

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[1] A. Atterberg, *Chem. Ztg.*, **21**. 261, 1897 ; *Zeit. anal. Chem.*, **36**. 214, 1897 ; L. Tietjens and Apel, *ib.*, **36**. 315, 1897 ; A. H. Allen, *B.A. Rep.*, 24, 1876 ; *Chem. News*, **35**. 259, 268, 1877 ; **36**. 17, 38, 47, 1877.

[2] With hydrogen gas (R. Finkener, *Pogg. Ann.*, **129**. 637, 1866); zinc dust (J. Diamant, *Chem. Ztg.*, **22**. 99, 1898); mercury (E. Sonstadt, *Journ. Chem. Soc.*, **67**. 984, 1895); magnesium ribbon (L. L. de Koninck, *Zeit. anal. Chem.*, **12**. 137, 1873 ; **21**. 406, 1882 ; C. Favre, *Compt. Rend.*, **122**. 1331, 1896 ; A. Villiers and F. Borg, *Bull. Soc. Chim.* (3), **9**. 602, 1893 ; A. Fiechter, *Zeit. anal. Chem.*, **50**. 629, 1911 ; R. Trnka, *ib.*, **51**. 103, 1912 ; A. Atterberg, *ib.*, **51**. 483, 1912); mercurous chloride (A. Mercier, *Bull. Assoc. Belg. Chem.*, **10**. 403, 1897); formic acid (H. N. Warren, *Chem. News*, **75**. 256, 1897) ; sodium formate (R. Böttger, *Zeit. anal. Chem.*, **13**. 176, 1874 ; F. Jean and J. A. Trillat, *Bull. Soc. Chim.* (3), **7**. 228, 1892 ; B. C. Corenwinder and G. Contamine, *Compt. Rend.*, **89**. 907, 1879 ; Woussen, *Ann. Agronom.*, **13**. 431, 1888) ; calcium formate (L. L. de Koninck, *Chem. Ztg.*, **19**. 901, 1895) ; sodium oxalate (F. Mohr, *Zeit. anal. Chem.*, **12**. 137, 1873 ; **21**. 216, 1883) ; thioacetic acid (A. Atterberg, *Zeit. anal. Chem.*, **36**. 314, 1897 ; *Chem. Ztg.*, **22**. 522, 538, 1898).

[3] J. Diamant, *Chem. Ztg.*, **22**. 99, 1898 ; A. Atterberg, *ib.*, **22**. 522, 538, 1898 ; L. L. de Koninck, *Zeit. anal. Chem.*, **35**. 72, 1896 ; F. Mohr, *ib.*, **12**. 137, 1873.

[4] Sufficient hydrochloroplatinic acid should be added to convert both the sodium and the potassium chlorides into the corresponding chloroplatinates. The solution of hydrochloroplatinic acid should contain 0·1 grm. of platinum per c.c. Assume that the mixed chlorides are all sodium chloride, multiply their weight by 17, and add 0·3 to the product. The result represents the number of cubic centimetres of the hydrochloroplatinic acid solution to be used. In the above example (page 225), 0·037 × 17 = 0·629 c.c. ; and 0·629 + 0·3 = 1 c.c. nearly. If sufficient hydrochloroplatinic acid has been added, a drop of the solution, under the microscope, will show golden yellow octahedral crystals of potassium chloroplatinate, and orange-coloured needles of sodium chloroplatinate. If colourless cubes of sodium or potassium chloride be present, insufficient hydrochloroplatinic acid has been added. The hydrochloroplatinic acid should be free from potassium and ammonium chloroplatinates. Potassium chloroplatinate is appreciably soluble in ammonium chloride (0·0015 grm. of potassium chloroplatinate dissolved in 10 c.c. of ammonium chloride solution). The importance of using pure hydrochloroplatinic acid has been emphasised by H. Vogel and H. Haefcke (*Lands. Ver. Stat.*, **47**. 97, 1896), H. Precht (*Zeit. anal. Chem.*, **18**. 509, 1879), A. F. Holleman (*Chem. Ztg.*, **16**. 35, 1892), and C. R. Fresenius (*Zeit. anal. Chem.*, **33**. 358, 1892). S. Zuckschwerdt and B. West (*Zeit. anal. Chem.*, **20**. 185, 1881) state that potassium chloroplatinate is soluble in hydrochloroplatinic acid, and consequently, if too great an excess of this acid be present, low results will be obtained. An excess, however, must be added to ensure complete precipitation. The comparatively small excess usually added cannot have an appreciable influence, even accepting Zuckschwerdt and West's data (100 c.c. of a solution of hydrochloroplatinic acid containing 7 grms. of platinum per 100 c.c. dissolve 0·3250 grm. of potassium chloroplatinate in 30 hours). W. Dittmar and J. McArthur (*Trans. Roy. Soc.*

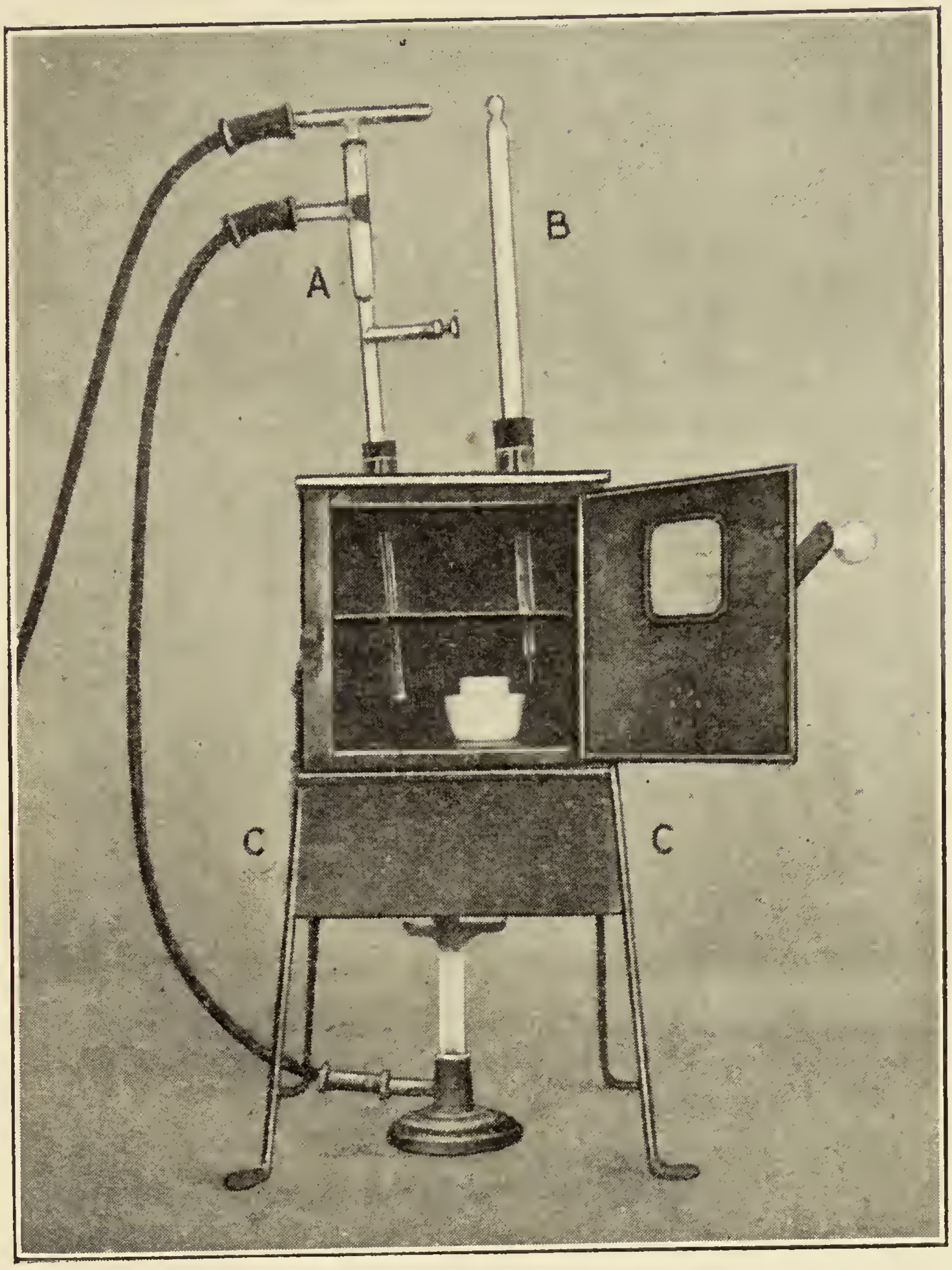

FIG. 116.—Air bath and thermostat.

Filtration and Washing.—Treat the residue with a few cubic centimetres of an 80 per cent. solution of alcohol.[4] Stir with a glass rod. Decant the liquid

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Edin., **33**. ii. 561, 1887 ; *Journ. Soc. Chem. Ind.*, **6**. 799, 1887 ; R. R. Tatlock, *Chem. News*, **30**. 71, 1874 ; **43**. 273, 1881) state that "the precipitate of potassium chloroplatinate has a remarkable tendency to carry down platinum chiefly as hydroxide, if produced in the absence of a large excess of hydrochloroplatinic acid." There appears to be a kind of hydrolysis in the dilute solution. For objections to sulphates with the "platinum chloride," see A. F. Holleman, *Chem. Ztg.*, **16**. 35, 1892.

[1] Sufficient water should be present to form a clear solution when first heated on the water bath.

[2] H. Precht, *Zeit. anal. Chem.*, **18**. 514, 1879. P. Rohland (*Zeit. anorg. Chem.*, **15**. 412, 1897 ; **16**. 306, 1898) does not recommend evaporation to dryness, since the dehydrated sodium chloroplatinate is less soluble in alcohol than the crystalline salt. G. Ulex (*Zeit. anal. Chem.*, **17**. 175, 1878) recommends adding 1 to 5 c.c. of a 20 per cent. solution of glycerol to prevent the sodium chloroplatinate becoming too dry, since otherwise it might not be dissolved. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2**. 290, 1905 ; Eng. edit., **2**. 220, 1900.

[3] The final result is independent of the kind of dish (platinum or porcelain) used in the evaporation ; the presence of a little free hydrochloric or sulphuric acid ; and the temperature of the water bath (A. L. Winton, *Journ. Amer. Chem. Soc.*, **17**. 453, 1895). Cases are on record where an insoluble platinous compound is formed by a reaction between the platinum of the dish and the salt. W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 422, 173, 1910.

[4] A. Mitscherlich (*Journ. prakt. Chem.* (1), **83**. 460, 1861) recommends adding the alcohol after the platinum salt, as indicated in the text.

through a weighed Gooch's crucible. Treat the mass again with 80 per cent. alcohol; and again decant. Repeat the decantations with 80 per cent. alcohol until the alcohol running through the Gooch's apparatus appears colourless; and the precipitate appears golden yellow, not orange yellow. Transfer the precipitate to the Gooch's crucible[1] by the aid of a "policeman." Wash with 80 per cent. alcohol by half filling the crucible about six times.

Drying the Precipitate.—Drain off the alcohol,[2] and dry the precipitate at 130° to a constant weight in an air bath whose temperature is maintained constant by means of a thermostat, *A*, fig. 116; or in an amyl alcohol bath, fig. 90. *B* represents the thermometer. The copper flange *CC* on the front and sides of the bath is to deflect the products of combustion from the flame up the back of the bath, away from the door. Cool the crucible in a desiccator, and weigh. The increase in weight represents the potassium chloroplatinate.[3]

Calculation.—Multiply the weight of the potassium chloroplatinate by 0·3068 (or see Table LXXXVII.) to get the corresponding amount of potassium chloride, and by 0·1941 (or see Table LXXXVIII.) to get the corresponding amount of potassium oxide. Subtract the amount of potassium chloride from the weight of the mixed chlorides in order to get the amount of sodium chloride in the given sample, and multiply the result by 0·5303 (or see Table LXXXIX.) to get the corresponding amount of sodium oxide. The following are the weighings obtained with half a gram of clay from which 0·0227 grm. of the mixed chlorides was obtained:—

Dish and mixed chlorides	26·2867 grms.
Empty dish	26·2640 grms.
Mixed chlorides	0·0227 grm.

Gooch's crucible and potassium chloroplatinate	27·6898 grms.
Gooch's crucible alone	27·6351 grms.
Potassium chloroplatinate	0·0547 grm.

Since 0·0547 × 0·3068 = 0·0168 grm. of potassium chloride,

Mixed chlorides	0·0227 grm.
Potassium chloride	0·0168 grm.
Sodium chloride	0·0059 grm.

Hence,

Weight of potassium chloroplatinate × 0·1941 = 0·0106 grm. K_2O.
Weight of sodium chloride . . × 0·5303 = 0·0031 grm. Na_2O.

If the amount of ammonium chloride and calcium chloride used in Smith's process for the mixed chlorides contained *a* grm. of K_2O, and *b* grm. of Na_2O, *a* must be subtracted from the potash, and *b* from the soda. A blank determination showed that the materials used in the above determination contained no potassium oxide ($a = 0$), but did contain ($b =$) 0·00022 grm. of Na_2O. Hence, the amount of sodium oxide is 0·0031 less 0·0002 = 0·0029 grm. per half gram of the clay. The clay in question thus contained the equivalent of 2·12 per cent. of K_2O, and 0·58 per cent. Na_2O.

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[1] The results are generally too high with tared filter papers—F. H. van Leent, *Zeit. anal. Chem.*, 40. 569, 1901; R. Caspari, *Zeit. angew. Chem.*, 6. 68, 1893; F. Bohm, *Zeit. anal. Chem.*, 38. 348, 1899; C. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 2. 290, 1905; Eng. edit., 2. 221, 1900; H. J. F. de Vries, *Chem. Weekblad*, 4. 231, 455, 1907; 5. 176, 1908.

[2] C. G. Eggertz and L. F. Nilson (*Königl. Land. Akad. Hand. Tids.*, 35. 326, 1898) here recommend drenching the precipitate with ether.

[3] According to H. Fresenius and P. H. M. P. Brinton (*Zeit. anal. Chem.*, 50. 21, 1911), if the weighed potassium chloroplatinate be caked into lumps, and not pulverulent, it should be redissolved in boiling water, and evaporated in a platinum dish on a water bath in which the water is not quite boiling, again dried at 130°, and weighed. The reasons will appear from page 233.

Errors.—Some idea of the magnitude of the accidental errors in the determination of the potash by this and Smith's process can be obtained from the following eight independent determinations made on one sample:—

0·0106; 0·0103; 0·0108; 0·0101; 0·0109; 0·0108; 0·0104; 0·0103.

The mean is 0·0105 grm. per 0·5 grm. of clay, that is, 2·10 per cent. The deviations range approximately between ± 0·04 grm. per 100 grms. of clay. It is necessary to mention that if the clay or silicate contained sulphur, and sulphur be not removed as indicated on page 226, some sodium sulphate is almost certain to contaminate the potassium chloroplatinate. In fact, the sulphates must be converted into chlorides by treatment with barium chloride before applying the "platinum" process. Care must be taken that there is no excess of either sulphate or barium chloride, or the results will be high.

§ 109. The Separation of Potassium as Potassium Perchlorate.

Potassium perchlorate is practically insoluble in concentrated alcoholic solutions, while sodium, barium, and magnesium perchlorates are soluble under the same conditions. In 1831, Sérullas[1] proposed a method for the determination of potassium based on this property, but owing to the difficulty in getting pure perchloric acid at that time, and to some mistaken ideas on the properties of perchloric acid, Sérullas' proposal did not get the attention it deserved. Quite satisfactory perchloric acid can now be easily obtained in commerce, and some of the principal sources of error have been investigated,[2] and methods devised by which results rivalling the hydrochloroplatinic acid process can be obtained, and this in less time and at a less cost—hydrochloroplatinic is uncomfortably expensive for commercial work. The greater simplicity of the process also renders it less liable to error when once the manipulation is mastered. The details of the method to be used in the separation are as follows:—

The Process.—Dissolve the mixed chlorides[3] in from 10 to 15 c.c. of hot water, and then add two or three times as much perchloric acid as is theoretically required to precipitate the mixed perchlorates. Evaporate the mixture on a water bath to a syrupy liquid until the fumes of perchloric begin to appear; cool a little. Take up the mass with hot water, and add 5 to 6 c.c. of perchloric acid. Re-evaporate until the fumes of perchloric acid again begin to appear.[1] The object of this treatment is to remove the hydrochloric acid. This is important. Stir the cold mass with about 20 c.c. of 96 or 97 per cent. alcohol containing 0·2 per cent. by weight of perchloric acid. Keep the potassium perchlorate as coarsely granular as possible. Let settle.[2] Decant through a dried and weighed Gooch's crucible. Wash the residue by decantation through the Gooch's crucible three times. About 20 c.c. of the alcohol will be needed for the washing. Transfer the precipitate to the Gooch's crucible by means of alcohol.[3] Some prefer to wash the residue at this stage with 20 c.c. of a mixture of equal parts of 97 per cent. alcohol and ether. Dry the precipitate at 120° to 130° for about half an hour,[4] and then weigh as $KClO_4$.

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[1] M. Sérullas, *Ann. Chim. Phys.* (2), **46**. 294, 1831.

[2] T. Schloesing, *Compt. Rend.*, **73**. 1269, 1871; K. Kraut, *Zeit. anal. Chem.*, **14**. 152, 1875; A. Bertrand, *Monit. Scient.* (3), **2**. 961, 1881; L. Grandeau, *Traité d'analyse des matières agricoles*, Paris, **1**. 419, 1897; D. A. Kreider, *Chem. News*, **73**. 8, 17, 1896; **72**. 241, 251, 261, 1895; *Zeit. anal. Chem.*, **9**. 343, 1870; D. A. Kreider and J. E. Breckenbridge, *ib.*, **13**. 161, 1897; *Chem. News*, **74**. 227, 1896; F. S. Shiver, *ib.*, **79**. 269, 281, 1899; *Journ. Amer. Chem. Soc.*, **21**. 33, 1899; R. Caspari, *Zeit. angew. Chem.*, **6**. 68, 1893; *Zeit. anal. Chem.*, **36**. 709, 1897; V. Schenke, *Landw. Ver. Stat.*, **47**. 36, 1895; C. Aumann, *ib.*, **60**. 231, 1901; A. Strigel and J. Dodt, *ib.*, **78**. 179, 1912; V. Schenke and P. Krüger, *ib.*, **67**. 145, 1907; W. Wense, *Zeit. angew. Chem.*, **4**. 691, 1891; **5**. 233, 1892; H. Kolbe, *Journ. prakt. Chem.* (2), **5**. 93, 1872; F. Hamel, *Chem. News*, **26**. 27, 1892; H. Precht, *International Cong. App. Chem.*, **7**. i, 146, 1909; G. Surr, *Min. Eng. World*, **36**. 605, 1912; W. A. Davis, *Chem. World*, **1**. 219, 1912; A. Wityn, *Russ. Journ. Exp. Agric.*, **2**. 192, 1912.

[3] The amount is calculated as follows:—Assume that the mixed chlorides are all sodium chloride, and that the perchloric acid used is 30 per cent. (sp. gr. 1·20) solution. Multiply the weight of the mixed chlorides by 6, and the product represents the number of cubic centimetres of acid required for the work. Perchloric acid of approximately 60 per cent. strength has a specific gravity of 1·54; 30 per cent., 1·20; and 20 per cent., 1·12. There is no difficulty about keeping the acid. It is not decomposed by hydrochloric or by sulphurous acid. The acid slowly volatilises at 138° without decomposition. It is not affected by exposure to light. The strength of the acid is easily determined by titration of a known amount with standard sodium hydroxide with phenolphthalein as indicator.

Calculations.—Assume that 0·5 grm. of clay has been treated by Smith's process, and that 0·0243 grm. of the mixed chlorides have been obtained.

Crucible and perchlorate	6·7223 grms.
Empty crucible	6·6951 grms.
Potassium perchlorate	0·0272 grm.

Multiply the weight of the potassium perchlorate by 0·5381 in order to find the equivalent amount of potassium chloride—or use Table LXXXVII. Hence,

$$0·0272 \times 0·5381 = 0·0146 \text{ grm. of potassium chloride.}$$

Multiply the weight of the potassium perchlorate by 0·33992 in order to find the equivalent amount of potassium oxide—K_2O—or use Table LXXXVI. Hence,

$$0·0272 \times 0·34 = 0·0092, \text{ or } 1·84 \text{ per cent. of } K_2O.$$

Subtract the weight of the potassium chloride from the weight of the mixed chlorides, and the result represents the weight of the sodium chloride.

Mixed chlorides	0·0243 grm.
Potassium chloride	0·0146 grm.
Sodium chloride	0·0097 grm.

Multiply the weight of the sodium chloride by 0·5303 in order to find the equivalent amount of sodium oxide—Na_2O—or use Table LXXXIX. Thus,

$$0·0097 \times 0·530 = 0·0052; \text{ or } 1·04 \text{ per cent. } Na_2O.$$

The Results.—The perchlorate process does its work fairly well in the presence of sulphates. Consequently it is not always necessary to remove the sulphates by means of barium chloride (page 226). Thus, with a mixture of potassium chloride and sulphate containing the equivalent of 0·0307 K_2O, Davis found

$$K_2O \ldots 0·0305;\ 0·0312;\ 0·0305;\ 0·0306;\ 0·0307;$$

and with 0·1 grm. K_2SO_4 containing 0·0541 grm. K_2O, Davis obtained 0·0536 and 0·0536 grm. K_2O. Quite correct results were also obtained with potassium chloride mixed with twice its own weight of sodium chloride, sodium phosphate, calcium chloride, or barium chloride. If phosphoric acid be present, a larger excess of perchloric acid is needed for the precipitation. Small amounts of magnesia do no particular harm, provided it is not present as sulphate when the precipitation is made; large amounts of magnesium salts give high results, and they must accordingly be first removed. Ammonium salts, if present, should be removed by boiling with sodium hydroxide, owing to the sparing solubility of ammonium perchlorate.

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[1] Some prefer to evaporate to dryness at this stage.

[2] The addition of a drop of ether aids filtration—E. Murmann, *Oester. Chem. Ztg.*, **13**. 227, 1910.

[3] A few drops of the filtrate, evaporated to dryness on platinum foil, should show no residue.

[4] Potassium perchlorate does not decompose below 400°.

§ 110. The Determination of Sodium Oxide.

It will be observed that the soda has been determined by difference, and, in consequence, the resulting error is the joint effect of the error in the determination of the mixed chlorides and in the determination of the potash. The two errors may exactly or partially neutralise one another, or they may act both in one direction. Hence, a comparison of the actual values obtained for the soda—Na_2O—in eight determinations of one sample of clay, indicated below, is particularly interesting:—

0·0029; 0·0030; 0·0034; 0·0035; 0·0030; 0·0029; 0·0031; 0·0030;

with a mean value of 0·0031 per half gram, and an error ranging between ± 0·0003. The theory of errors furnishes a value for the error ± 0·00035 which is very near the value actually obtained when the soda—Na_2O—is determined by difference. The accidental errors per 100 grms. of clay do not differ much from ± 0·03 grm. Hence, this method of finding the amount of sodium oxide in a clay is quite reliable, and there is no need to determine the soda directly. Indeed, the direct processes at present available are somewhat risky and offer no advantage over the difference method.

The soda can be determined directly in the filtrate from the potassium chloroplatinate by evaporating the filtrate to a small volume, and reducing the platinum to metal by means of formic acid. Filter off the platinum; evaporate to dryness in a weighed dish; and finally weigh as sodium chloride,[1] or as sodium sulphate.[2]

Determination as Sodium Antimoniate.—Beilstein and Blaese[3] recommend the following direct process for sodium:—Add a solution of potassium antimoniate to a solution of the mixed chlorides or nitrates, not carbonates, and let the mixture stand 24 hours in the cold. Decant the clear liquid through a Gooch's crucible, and wash the precipitate with a solution of potassium acetate (7 grms. per litre), and finally with 50 per cent. alcohol. Calcine the precipitate, and weigh as $NaSbO_3$. In order to correct the result for solubility of the sodium antimoniate, add 0·0233 grm. to the weight of the precipitate for every 100 c.c.

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[1] Some of the lithium in the silicate will be found with the sodium chloroplatinate in the filtrate (page 236); most will be precipitated with the carbonate in removing lime and magnesia by Gooch and Eddy's process, but not by Smith's process. Most of the cæsium and rubidium, if present, will be found with the potassium, since both cæsium and rubidium chloroplatinates are even less soluble than the corresponding potassium salt—W. Crookes, *Chem. News*, **9.** 37, 205, 1864; R. Bunsen and G. Kirchhoff, *Pogg. Ann.*, **113.** 337, 1861; *Zeit. anal. Chem.*, **1.** 62, 1862; R. Bunsen, *ib.*, **2.** 161, 1863. For the separation of the three chloroplatinates, see O. D. Allen, *Amer. J. Science* (2), **34.** 367, 1862; *Zeit. anal. Chem.*, **2.** 68, 1863; *Chem. News*, **6.** 265, 1862. F. Stolba's process (*Zeit. anal. Chem.*, **12.** 440, 1873) with stannous chloride is not good; while F. Godeffroy's process (*Ber.*, **7.** 375, 1876) with antimony chloride is very fair (A. Cossa, *Acad. dei Lincei* (3), **2.**). H. C. Wells, *Amer. J. Science* (3), **43.** 17, 1892; (3), **46.** 186, 1893; H. H. Johnson and O. D. Allen, *ib.* (2), **35.** 94, 1863.

[2] A. Mitscherlich, *Zeit. anal. Chem.*, **1.** 59, 1862; G. Werther, *Journ. prakt. Chem.* (1), **91.** 321, 1864.

[3] F. Beilstein and O. von Blaese, *Bull. Acad. Sciences St. Pétersbourg*, **33.** 209, 1895.

of the mother liquid, not washing fluid, which is in contact with the precipitate. I have had very little experience with the method. I am told by an analyst who has tested the process that it is unsatisfactory for general work. I have had no experience with Ball's process of separation based on the insolubility of sodium bismuthi-nitrate.[1]

§ 111. The Preparation of Hydrochloroplatinic Acid from Platinum Residues and Scraps.

Although usually called platinum chloride—$PtCl_4$—the reagent employed for separating potassium in the form of potassium chloroplatinate is really hydrochloroplatinic acid—H_2PtCl_6. In order to keep down expenses, it is very necessary to collect all platinum residues, alcoholic washings, platinum scraps, etc., in bottles provided for the purpose, and then to recover the platinum at convenient intervals. The recovered platinum is usually converted into hydrochloroplatinic acid.[2]

1. *Alcoholic Washings.*—Distil off the alcohol[3] and take up the residue with water;[4] add the potassium chloroplatinate residues to the solution. Pour the solution into a solution of sodium hydroxide[5] mixed with 8 per cent. of glycerol. Heat the solution to boiling, and the platinum separates as a heavy black powder. Wash with water, then with hydrochloric acid, and then with water again. Dry. Ignite the powder in order to destroy organic compounds, and weigh.

2. *Platinum Scraps.*—These may contain iridium, which is itself insoluble in aqua regia, but soluble in this menstruum when alloyed with platinum. Dissolve the platinum in aqua regia ($3HCl + HNO_3$) in a capacious flask on a water bath. When solution is complete, evaporate to a syrupy consistency in a large porcelain basin. Take the residue up with water, and gradually add sodium carbonate and sodium formate until the solution is alkaline.[6] Heat to boiling. Both platinum and iridium are precipitated as black powders. Decant off the supernatant liquid. Wash the residue with dilute hydrochloric acid to remove sodium salts, and then with water to remove the acid. Dry the powder,

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[1] W. C. Ball, *Journ. Chem. Soc.*, **97**. 1408, 1910.

[2] L. Opificus, *Zeit. anal. Chem.*, **23**. 207, 1884; H. Precht, *ib.*, **18**. 509, 1879; G. Krause, *ib.*, **14**. 184, 1875; W. Dittmar and J. M'Arthur, *Trans. Roy. Soc. Edin.*, **33**. ii., 561, 1887; H. C. Weber, *Journ. Amer. Chem. Soc.*, **30**. 29, 1908; W. C. Zeise, *Pogg. Ann.*, **21**. 498, 1830; **40**. 234, 1837; E. Duvillier, *Compt. Rend.*, **84**. 444, 1877; T. Knösel, *Ber.*, **6**. 1159, 1873; H. W. Wiley, *Journ. Amer. Chem. Soc.*, **19**. 258, 1897; *Chem. News*, **75**. 214, 1897.

[3] Purification of Alcohol.—The alcohol may be recovered by re-distilling from quicklime. Put 1½ litre of alcohol in a 2-litre Winchester, add 180 grms. freshly burnt quicklime in coarse powder. Agitate every now and again for about 8 days. Distil the alcohol into a large flask. Add about 120 grms. freshly burnt quicklime per litre. The alcohol which is distilled from this will be very nearly absolute—J. L. Smith, *Chem. News*, **30**. 234, 1874. The alcohol may then be mixed with powdered potassium permanganate until it is distinctly coloured; allow to stand some days until the permanganate is decomposed, and manganese oxide is deposited. Add a little quicklime, and distil slowly. When 10 c.c. of the distillate gives no perceptible yellow coloration when boiled with 1 c.c. of a concentrated solution of caustic soda or potash, the subsequent distillate is collected for use. The alcohol so obtained is neutral, and gives no coloration on boiling with silver nitrate or caustic alkalies—E. Waller, *Journ. Amer. Chem. Soc.*, **11**. 124, 1889.

[4] On evaporating the solution of hydrochloroplatinic acid to dryness in the presence of alcohol, hydrochloroplatinous acid—H_2PtCl_4—and ethylene are formed. These react to produce ethylene platinous chloride, which dissolves in alcohol, forming an explosive powder when evaporated to dryness. The dry powder is insoluble in acids.

[5] 21 grms. of sodium hydroxide made up to 100 c.c. with water. Add 8 to 10 c.c. of glycerol.

[6] Take care that there is no loss by spurting during effervescence.

and ignite in a weighed porcelain crucible over a blast lamp, whereby the iridium becomes insoluble in aqua regia. Weigh.

Conversion of the Metal into Hydrochloroplatinic Acid.—Dissolve the grey powder at as low a temperature as possible in hydrochloric acid, and add nitric acid in small quantities at a time. In this way some nitrosoplatinic chloride—$PtCl_4(NO)_2$—is formed. This must be destroyed, since it leads to low results in the determination of potassium. Evaporate the solution with water, whereby the nitrosoplatinic acid is decomposed into hydrochloroplatinic acid with evolution of nitrogen oxides. Some of the latter still remain in solution. Hence, add more water and hydrochloric acid, and again evaporate. These operations are repeated until no more nitrous fumes are evolved.[1] During these operations, some hydrochloroplatinous acid is formed—H_2PtCl_4. This is particularly objectionable, since it leads to high results when the chloroplatinic acid is used for the determination of potassium. In order to convert hydrochloroplatinous into hydrochloroplatinic acid, saturate the warm solution with chlorine gas, and evaporate the solution at as low a temperature as possible to a syrupy consistency. Dissolve the yellowish-brown mass in water (cold), and if any insoluble iridium be present, filter, wash, ignite, and weigh the residue. Subtract the result from the weight of metal taken. The difference gives the amount of platinum which has passed into solution. Dilute the solution until it contains the equivalent of 1 grm. of platinum (metal) per 10 c.c.

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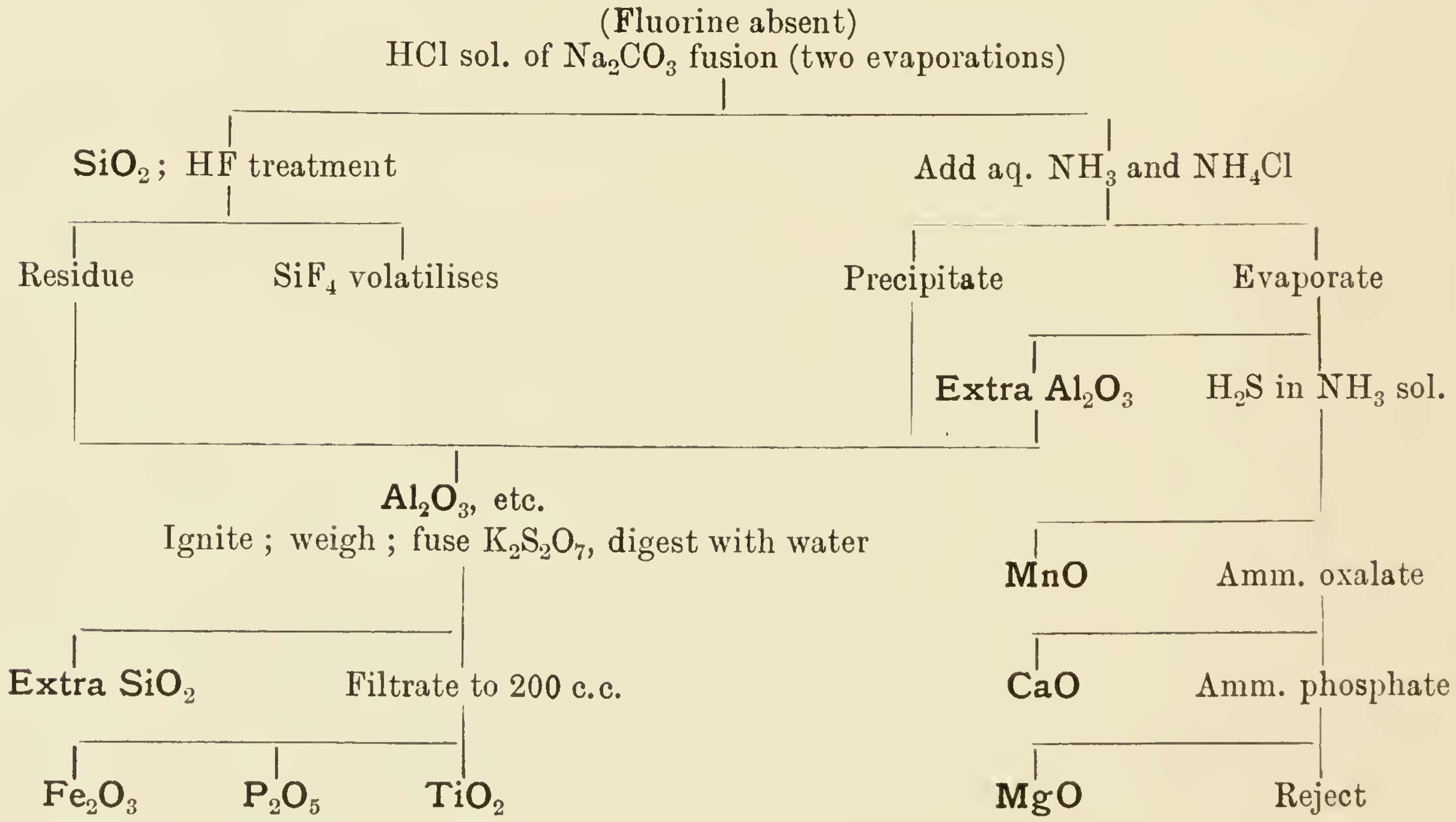
[1] W. Dittmar and J. M'Arthur (*l. c.*) doubt if it is possible to destroy all the nitrosoplatinic chloride in this manner. They recommend acting on the metal with hydrochloric acid and chlorine from a "chlorine Kipp." H. Precht (*Zeit. anal. Chem.*, **18**. 509, 1879) and W. A. Noyes and H. C. P. Weber (*Journ. Amer. Chem. Soc.*, **30**. 13, 1908) have also emphasised the necessity for removing nitric acid from the hydrochloroplatinous acid. J. S. Stas (*Chem. News*, **73**. 5, 1896) removes the chlorine by dissolving the salt in water; raises the temperature of the solution to its boiling point; saturates the solution with chlorine; and keeps the temperature of the solution at 100° until it ceases to smell of chlorine.

CHAPTER XVIII.

ABBREVIATED ANALYSES AND ANALYTICAL ERRORS.

§ 112. Exhaustive *v.* Works Analyses.

It will now be well to review our results. The hydrochloric acid solution of the sodium carbonate was evaporated twice, with an intervening filtration, and the silica filtered off, ignited, weighed, and treated with hydrofluoric acid. The filtrate was precipitated twice with ammonia and ammonium chloride. The precipitate was ignited with the residue from the silica, and weighed as a mixture of aluminium, ferric, titanic, and phosphoric oxides. This was fused with potassium pyrosulphate, the insoluble silica filtered off, and the solution made up to 200 c.c. Of this, 50 c.c. were used for the determination of iron colorimetrically; and 100 c.c. for the titanic oxide.[1] The filtrate from the alumina was evaporated down to a small bulk, and alumina separated in the usual way.[2] The filtrate was treated with ammonium oxalate. The precipitated calcium oxalate was filtered off; and the filtrate was treated with ammonium sodium phosphate, when a precipitate of magnesium phosphate was obtained. The next filtrate was rejected. The alkalies were determined on a separate sample. Summarised (solids to left, solutions to right) :—



It is important in devising analytical schemes to keep the object of the analysis clearly in view. If extreme accuracy be desired for research and other purposes, no precautions must be neglected which will ensure exact results. The analysis may have to be criticised while the analyst is in the witness box in the County Court. In such cases he must be prepared to furnish clear, concise, complete, and conclusive proofs of the accuracy of his statements. The purity of the reagents should have been established by blank or other tests; and the degree of accuracy of the analytical process should be known. Analyses for reports on new clays, etc., usually call for more exhaustive details than are needed for general practice.

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[1] And, if desired, 100 c.c. for the phosphorus (page 595).

[2] The solution can then be treated with ammonia and hydrogen sulphide to precipitate the manganese sulphide (*q.v.*).

If the analysis is to be made for industrial work, accuracy *and* speed are of prime importance. Such precautions must be adopted as will ensure the required degree of accuracy. Ultra-refined processes waste time. *Superfluitas*, said Bacon, *impedit multum et reddit opus abominabile.* A scheme of analysis might serve a given purpose admirably, and yet appear grotesque if applied with another object in view. The determination of the 0·03 per cent. of lithia usually present in Cornish stone, for instance, would be useless for ordinary technical requirements. We should not know how to apply the information if we had it. A certain amount of care is imperative in applying the principle, "near enough for our purpose," because unsuspected sources of faults, etc., might easily be overlooked.

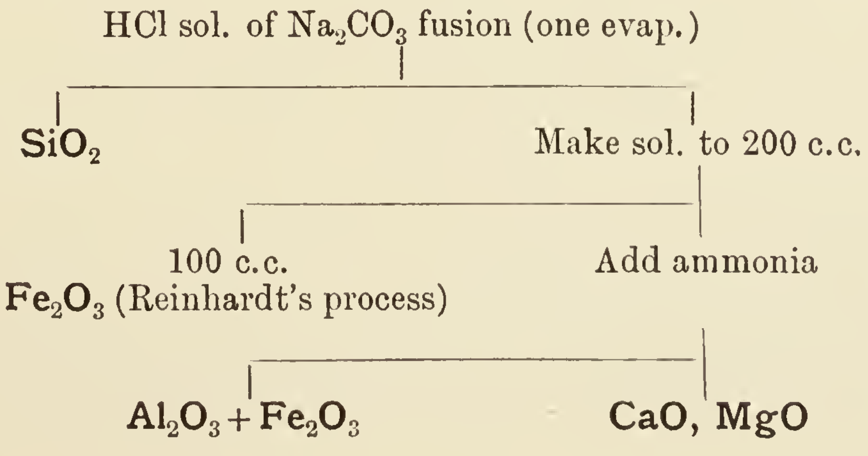
The prime object of chemical analysis in industrial practice is to prevent errors of commercial importance. These errors may arise from (1) a variation in the composition of the raw materials; (2) a wrong proportioning of the clays in a body mixture, etc.; (3) the need for checking the efficiency of processes of purification, grinding, etc., at different stages in the manufacture; (4) the introduction of deleterious impurities with the raw materials; (5) payment for raw materials invoiced, possibly, higher than their market value; etc.

§ 113. Abbreviated Schemes of Analysis.

In purchasing raw materials, the analysis must frequently be conducted in a much shorter time than is possible by the scheme indicated in the preceding pages. The necessary time is not available, and an exact analysis may be no more useful than a close approximation. The material may have been sold before the analyst has completed his work. The analysis, when completed, is accordingly useless for his own firm—a rival has bought the material.

The methods of analysis taught in the schools are not those which have developed under the stress of competitive practice. The analytical chemist must therefore exercise his analytical faculties, not only in manipulative skill, but also in distinguishing between necessary precautions and unnecessary exercises in chemical gymnastics. The two faculties are not always located in the same man. The one is mere mechanical dexterity; the other is the quality which makes a man valuable.

Simplified Scheme of Analysis.—A simpler scheme suitable for certain analyses in routine work may be employed for many purposes. This will be understood from the following representation (solids to left, solutions to right):—



For simply checking the correctness of a "mixing," the determination of the silica may suffice. In some cases a mere determination of the loss on ignition of the dried (110°) sample will show whether it is necessary to proceed further with the analysis. The idea is to pick out one or two components which admit of easy determination—lead and lime, for instance, in a glaze. If these be quite normal, it is sometimes sound reasoning to infer that the different constituents have been properly proportioned.

Rapid Clay Analyses.—It is possible to determine the silica, alumina, and ferric oxide in a clay without using a platinum crucible, and in a comparatively short time, by the following process:—[1]

Mix 0·5 grm. of the clay with six times its weight of "peroxide fusion mixture"[2] in a 30-c.c. nickel crucible with a nickel spatula. Fuse the mass for about 5 minutes at a dull red heat.[3] Cool. Place the crucible in an evaporating basin 12 cm. diameter, or in a covered beaker. Add water slowly. The action may be somewhat vigorous, and care must be taken to avoid loss by spurting. The heat generated during the action will lead to a rapid dissolution of the cake. Add an excess of hydrochloric acid. Evaporate the solution to dryness. Grind the residue to powder. Dehydrate the mass at about 110° for an hour. Digest the mass with hydrochloric acid; filter; wash and ignite the residue in a porcelain crucible for total silica. Make the filtrate up to 200 c.c.

Precipitate the aluminium and ferric hydroxides in 100 c.c. of the solution by adding an excess of ammonia in the usual manner, and weigh as mixed $Al_2O_3 + Fe_2O_3$. Determine the ferric oxide in the other 100 c.c. by Reinhardt's process. All this involves 3 or 4 hours' work, excluding the 2 to 4 hours required for the evaporation of the silica.[4] Hence two such partial analyses can be made in a day.

§ 114. The Indirect Determination of Lime and Magnesia.

The lime and magnesia can be determined much more quickly by the indirect process than by precipitation respectively as oxalate and as ammonium magnesium phosphate.

Schaffgotsch[5] showed that calcium and magnesium carbonates separate from a solution containing a great excess of ammonium carbonate and ammonia, probably in the form of double ammonium carbonates. A certain amount of magnesium carbonate is, however, hydrolysed under these conditions, and the precipitation of the magnesia is not therefore quite complete. Gooch and Eddy[6] have shown that the separation is completed in a relatively short time if the solution contains an excess of alcohol.

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[1] See E. P. Fleming, *Western Chem. Met.*, **5.** 396, 1909; J. H. Walton, *Journ. Amer. Chem. Soc.*, **29.** 481, 1907. See E. Ladd, page 460.

[2] PEROXIDE FUSION MIXTURE.—Mix 4 parts by weight of the purest sodium peroxide with 1 part of the purest sodium hydroxide. Sodium peroxide usually contains traces of silica. The amount can be determined by a blank experiment and an allowance made for the 3 grms. of peroxide fusion mixture used.

[3] For a still more rapid method of decomposition, see page 267.

[4] For systems of accelerated evaporation, see H. J. S. Sand, *Journ. Soc. Chem. Ind.*, **26.** 1225, 1907; W. Hempel, *Ber.*, **21.** 900, 1888; C. Jones, *Journ. Anal. App. Chem.*, **3.** 121, 1889; R. Fessenden, *Chem. News*, **61.** 4, 1890; E. Donath, *Chem. Ztg.*, **32.** 1107, 1908; T. Brugnatelli, *Gaz. Chim. Ital.*, **16.** 1878; J. W. Gunning, *Zeit. anal. Chem.*, **26.** 725, 1887; A. Gawalovski, *ib.*, **12.** 181, 1873; C. Zengelis, *ib.*, **45.** 758, 1906.

[5] F. C. Schaffgotsch, *Pogg. Ann.*, **104.** 482, 1858; **106.** 294, 1859; A. K. Christomanos, *Zeit. anal. Chem.*, **42.** 606, 1903. See page 227.

[6] F. A. Gooch and E. A. Eddy, *Amer. J. Science* (4), **25.** 444, 1908; *Chem. News*, **97.** 280, 1908; J. M. Stillman and A. J. Cox, *Journ. Amer. Chem. Soc.*, **25.** 732, 1903; E. Dreschel, *Journ. prakt. Chem.* (2), **16.** 169, 1878; O. Foote, *Gaz. Chim. Ital.*, **24.** i, 207, 1894. According to O. Bertrand (*Monit. Scient.* (3), **10.** 477, 1880), at 10°, 1 part of calcium carbonate

Determination of the Mixed Oxides.—After the sodium carbonate fusion, the silica and alumina have been removed in the usual manner, and the filtrate from the alumina is boiled down to a small volume,[1] and an equal volume of alcohol and 50 c.c. of Gooch and Eddy's solution (page 227) added. In about half an hour the precipitate is washed with the same solution, and dissolved in a small volume of dilute hydrochloric acid; neutralised with ammonia; and an equal volume of Gooch and Eddy's solution and alcohol added. The precipitate is washed as before, ignited in a weighed platinum crucible, and weighed as a mixture of $CaO + MgO$.[2]

Transformation of the Mixed Oxides to Sulphates.—Add, very carefully, sufficient dilute sulphuric acid[3] to combine with all the lime and magnesia in the crucible. Evaporate the solution to dryness; gradually raise the temperature of the crucible to the full heat of a Bunsen's burner[4] for about a quarter of an hour Weigh[5] the contents of the crucible as mixed $CaSO_4 + MgSO_4$.

Calculations.—Suppose that W represents the weight of the mixed oxides, w the weight of the mixed sulphates; then, if u represents the weight of the SO_3 present, $w - W = u$. By the method of page 229, therefore, we have the two equations:

$$MgSO_4 + CaSO_4 = w; \quad \text{and} \quad 0{\cdot}665\ MgSO_4 + 0{\cdot}588\ CaSO_4 = u.$$

Hence,

$$CaSO_4 = 8{\cdot}6363w - 12{\cdot}987u; \quad MgSO_4 = w - CaSO_4.$$

In illustration, suppose the mixed oxides weighed 0·0265 grm., and the mixed sulphates 0·0703 grm., it follows that the mixture contains 0·0383 grm. of $CaSO_4$ and 0·0320 grm. of $MgSO_4$. But

$$CaSO_4 \times 0{\cdot}412 = CaO; \quad \text{and} \quad MgSO_4 \times 0{\cdot}335 = MgO.$$

Hence, the given mixture has 0·0160 grm. CaO, and 0·0107 grm. MgO.

§ 115. Permitted Errors.

If all the constituents in any given silicate have been determined, the numbers, in the ideal case, should add up to 100 per cent. The proximity of the actual sum to the ideal 100 is a valuable check on the accuracy of the work. Absolute identity would not represent perfect work.[6] The errors due to incomplete washing; dust; inevitable impurities in the best of reagents; action of the reagents and solutions on the glass and porcelain, etc., all tend to make the

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is soluble in 13,980 parts of water containing ammonium chloride; in 8380 parts of water containing ammonium sulphate; and in 14,438 parts of water containing ammonium nitrate.

[1] If alumina separates, it must be of course filtered off.

[2] If baryta and strontia be present, they will be included with these bases. To evaluate the mixture by a titration process, see A. Trabert, *Compt. Rend.*, **119**. 1009, 1894; *Chem. News*, **71**. 26, 1895.

[3] The addition of sulphuric acid is not a very safe operation for an analytical process. It is best to add an ammoniacal solution of ammonium sulphate containing a little ammonium chloride—W. L. Scott, *Chem. News*, **1**. 144, 1860.

[4] If no fumes of sulphuric acid came from the crucible when it was being ignited at the higher temperature, insufficient sulphuric acid was probably added. In that case, more sulphuric acid must be added when the crucible has cooled. A large excess of sulphuric acid should be avoided.

[5] The mixture is a little hygroscopic, and must not be needlessly exposed to the air before weighing.

[6] F. Jordis, *Zeit. anorg. Chem.*, **45**. 362, 1905. If the weighings be not all reduced to "weight *in vacuo*," it is easy to prove that the sum of the several constituents with ordinary analytical weights, and with *perfect* work, cannot add up to 100. The proof is easy to see from § 10, page 23. The clay is weighed with, say, a 1-grm. brass weight, the other constituents of the clay with platinum weights. The difference is illustrated in Table V., page 23.

total greater than 100. On the other hand, mechanical losses through imperfect cleaning of the vessels in transferring liquids and solids from one vessel to another; accidental spilling of drops; the slight solubility of the precipitates, etc., all tend to reduce the total below 100 per cent. There is but a remote probability—perhaps exceeding one in a hundred—that the two sets of errors will exactly balance one another, and the ideal 100 be obtained. The coincidence would be mere chance, and when it does occur it may be somewhat embarrassing. It is necessary to decide on limiting deviations above and below 100 for satisfactory work. If these limits be exceeded, the analysis is to be condemned. Hillebrand[1] places these limits at 99·75 and 100·5; Washington[2] prefers 99·5 and 100·75. If the total falls below 99·5, there is strong presumptive evidence that some constituent has been either overlooked or ignored. In the analysis of clays for technical purposes no pretence is made to exhaust the possible constituents. Only those constituents of technical importance are determined. Hence, it is advisable to extend the lower limit. In reports on clays and related materials I make ± 0·5 the permitted limiting deviations from 100. If the total falls below 99·5, it is advisable to find the missing constituent. If the analysis pretends to be exhaustive, the lower limit should be raised.

The practice of adjusting the results of an analysis to an exact 100 is utterly bad—although it rather appeals to a business man who is ignorant of what is implied, and likes to see the data "properly balanced," as he calls it. Apart altogether from the ethics of the computation, and the temptation to "cook" a defective analysis, the adjustment, as Fresenius[3] has pointed out, "prevents others from judging the accuracy of the results," and, in consequence, makes chemists reasonably sceptical as to the value of the work. The figures must always be given as they are obtained, and it is just here that the integrity of the analyst meets its first test.[4] There is an impression that a satisfactory summation is a sufficient criterion of accurate work. As a matter of fact, *a satisfactory summation is no proof that the separations have been correctly performed.* This is well demonstrated by the ratio $SiO_2 : Al_2O_3$ in different analyses of the same clay by different men.[5]

Another meretricious system of reporting commercial analyses may be illustrated by quoting the last three lines of an analysis of ball clay from a "clay expert's" report:—

. . . .	.
Alkalies	1·83
Undetermined constituents	0·18
Total	100·00

The "undetermined constituents" will not deceive a chemist who has grasped the significance of the errors incidental to all methods of analysis, but it may mislead[6] those who have not devoted special attention to the subject.

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[1] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **305**. 26, 1907.

[2] H. S. Washington, *Manual of the Chemical Analysis of Rocks*, New York, 24, 1904. For the limits of accuracy in the analysis of alloys, see E. A. Lewis, *Metal Ind.*, **2**. 304, 1910; *Journ. Soc. Chem. Ind.*, **31**. 96, 1912. See also J. Grossmann, *ib.*, **18**. 977, 1896.

[3] R. Fresenius, *Quantitative Chemical Analysis*, London, **2**. 101, 1900.

[4] Clay analyses have been published where the total number of constituents makes over 104 per cent., and that not a misprint. We cannot but admire the honesty of the analyst—a professional, by the way. The work should have been repeated. Its publication was ill-advised.

[5] Of course, something is then wrong. If baryta were overlooked in a glaze analysis, the "total" might be satisfactory, and yet the alumina, tin, etc., might be high, especially if sulphates be present.

[6] "100 per cent. analyses" are frequently "crocks." As a matter of fact, there was a discrepancy between the above result and the vitreous qualities of the clay. Another analyst reported 3·0 per cent. potash (K_2O), and 1·8 per cent. soda (Na_2O). This corresponds with 4·8 per cent. alkalies, and agreed with the known properties of the clay. For "alkalies" see page 222.

Dittrich[1] has analysed artificial mixtures containing known quantities of the principal constituents which occur in silicate rocks, and found the limits of error[2] to be as follows:—

Table XLIII.—Accidental and Constant Errors in Silicate Analyses.

Constituent.	Limits (per cent.).
Alumina	− 0·15 and − 0·25
Ferric oxide	+ 0·2 and − 0·3
Lime	− 0·1
Magnesia	− 0·1
Potash (Bunsen's process) . .	+ 0·1
Potash (Smith's process) . .	− 0·1 and − 0·2
Soda (Bunsen's process) . .	+ 0·2 and − 0·3
Soda (Smith's process) . . .	− 0·1 and − 0·2

Each limit will naturally vary with the skill of the analyst, with the process of analysis, and be dependent upon the number of separations involved in the analysis. In general, *the greater the number of separations, the greater the errors of the analysis.*

In order to find what accidental errors might be expected in clay analyses, eight independent analyses of one homogeneous sample of clay were made in my laboratory by an analyst accustomed to work with the processes recommended in this book. Details have been indicated in the preceding text. The results are here collected in Table XLIV.

Table XLIV.—Accidental Errors in Eight Analyses of a Clay.

Constituent.	Mean values per cent.	Maximum and minimum deviations.
Silica	60·47	±0·07
Titanic oxide . .	1·20	±0·07
Alumina . . .	21·90	±0·10
Ferric oxide . .	1·50	±0·06
Lime	1·45	±0·08
Magnesia . .	1·10	±0·08
Potash . . .	2·11	±0·04
Soda	0·62	±0·04
Loss on ignition .	9·30	±0·05

The above numbers take no account of constant errors. Dittrich's Table XLIII. indicates both constant and accidental errors. The errors would be different if different amounts of each constituent were present, and different methods of analysis employed. *The relative error involved in separating a relatively small amount of a constituent is greater than in separating a large quantity,* because, in the former case, a small quantity of impurity and the slight solvent action of the mother liquid have a greater influence on the final result. The sulphur and chlorine have not here been determined; without these, and certain other constituents, the total is 99·59 per cent. This series of analyses, with some hundreds of other analyses, have led me to place the check for commercial analyses at 100 ± 0·5, as indicated above.

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[1] M. Dittrich, *Neues Jahrb. Min.*, **2.** 69, 1903.

[2] By "accidental error" is understood the irregular deviations from the arithmetical mean which are just as likely to have a positive as a negative value. A "constant error" is an error due to well-defined causes which make the error incline more in one direction than in another —*e.g.*, errors due to a defect in the pipette, burette, measuring flask, solubility of precipitate, etc. The correction tables pages 29 and 49 are intended to neutralise constant errors due to the causes named. For a discussion on accidental and constant errors, see J. W. Mellor, *Higher Mathematics for Students of Chemistry and Physics*, London, 510, 537, 1909. The accuracy of the results can be expressed in several different ways, *e.g.*: "the results are within, say, 0·1 of each other"; "the results are accurate to ±0·1 per 100 parts of the sample"; "the results are accurate to ±0·1 per 100 parts of the given constituent in the sample"; etc.

It will be obvious that if each constituent had its maximum deviation, or if each constituent had its minimum deviation, the total might fall outside the assigned limit, and the analysis be condemned although the error with no constituent exceeded the tolerated limits. The chance of this event happening is over 1 in 100,000,000 analyses. The magnitude of the errors might be reduced by working in a clearer atmosphere than sometimes prevails in the testing laboratory of a works,[1] and using platinum utensils. The numbers given above represent analyses made under routine conditions by the method described in what precedes.

The Committee of the American Chemical Society "On Uniformity in Technical Analysis"[2] reported the results of 35 analyses of one sample of an argillaceous limestone made by different laboratories. These are somewhat startling in their want of agreement. I have given the mean of two concordant analyses by the two referees in the second column of the table, and the maxima and minima results sent to the committee by the different analysts in the last two columns.

Table XLV.—Comparative Analyses of an Argillaceous Limestone.

Constituent.	Standard.	Minimum.	Maximum.
Silica . . .	18·14	16·58	18·92
Titanic oxide . .	0·22	0·11	0·82
Alumina . . .	5·70	4·42	7·35
Ferric oxide . .	1·71	1·06	2·83
Manganese oxide .	0·04	none	1·70
Lime . . .	37·65	35·26	41·98
Magnesia . .	1·93	0·92	3·05
Potash . . .	1·14	0·46	2·68
Soda . . .	0·33	0·11	2·00
Loss on ignition .	32·27	31·94	32·88
Phosphoric oxide .	0·18	0·12	0·65
Sulphur . . .	0·27	none	0·71
Sulphur trioxide .	0·012	none	0·69
Carbon . . .	0·64	0·41	2·03
Carbon dioxide .	30·68	28·65	31·65

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[1] I am here reminded of a quaint explanation, given by the *Brit. Clayworker*, **19**. 155, 1910, of the fact that two analyses of a clay differed in the amounts of silica and iron. The one with the higher silica was made by a clay analyst, the one with the higher iron by an iron and steel works analyst. The claim was made that the iron in the latter case was high because the utensils of the iron and steel analyst were probably contaminated with iron. The *tu quoque* retort might have been made with reference to the silica of the clay analyst.

[2] *Journ. Amer. Chem. Soc.*, **26**. 1652, 1904; **28**. 223, 1906. See also "Report of the Subcommittee on the Uniformity in Analysis of Materials for the Portland Cement Industry," *Journ. Soc. Chem. Ind.*, **21**. 12, 1223, 1902; H. W. Stanger, **21**. 1216, 1902.

§ 116. The Chief Sources of Error in Analyses.

> Every careless step in an analysis shows itself in material mistakes. The student must reason closely to keep his solutions correct. He cannot go on long with mere enthusiasm and boasting. His own results bring him the greatest reproaches. His experiments silently humble him, and he is laughed at by the forces which he cannot avenge.—W. CROOKES.[1]

It may be here instructive to follow Jüptner's plan and summarise the more important sources of error.[2] Most of these have already been discussed in detail.

(1) *Imperfections in sampling.*—This, as already indicated, is a prolific source of discrepancies in analytical results.

(2) *Errors due to mistakes and lack of skill.*—Mixing the samples; arithmetical errors in calculations; wrong reading of burettes, weights, tables; sticking of Erdmann's float; dirty vessels; etc. The susceptibility of a worker to errors of this kind is greater in badly equipped laboratories, imperfect illumination; overwork, with consequent fatigue and lapses of attention, and with a laboratory near a dusty road. Experiments with clays favour the development of dust, and clay dust settling in beakers, funnels, etc., conduces to high results.

(3) *Impure reagents.*—Phosphates in ammonium nitrate used for washing the alumina and the ammonium phosphomolybdate precipitates; iron and carbon in the zinc used for reducing ferric salts for the permanganate titration; fluorine in the hydrogen peroxide used for the titanium determinations; silica in the sodium carbonate flux; alkalies in the calcium carbonate used in Smith's process; vanadium in the potash; chlorides or sulphates in the sodium carbonate or nitrate; etc.

(4) *Faulty measuring apparatus.*—The weights may be in error; the volumetric apparatus may not be consistent; the volumetric measurements may not be corrected for variations of temperature; etc.[3]

(5) *Errors in manipulation.*—Action of water on the glass vessels; introduction of sulphur from rubber stoppers used in sulphur determinations; moisture in the apparatus used in fluorine determinations; losses by spitting when an alkaline carbonate is neutralised by an acid; etc.

(6) *Errors due to faults in the process of analysis.*—Examples occur during the precipitation of barium sulphate (page 618); incomplete oxidation of carbon in the wet combustion process (page 546); solubility of silica (page 186); adsorption of salts by precipitates—*e.g.*, the "alumina" precipitate, and by the calcium carbonate in the Smith's process for alkalies; the solvent action of hydrochloric acid on sulphides—*e.g.*, lead sulphide.

(7) *Personal errors.*—Defects in the perception of colour in colorimetric processes; methods of reading burette; method of adding reagents to solutions (page 178); etc. The result is that one chemist gets consistently better results with one process than with another, whereas the converse may be true for another chemist.[4] The differences of opinion as to the relative merits of the cyanide, iodine, and electrolytic processes for copper might be cited in illustration. By studying the properties of precipitates, the number of filtrations, and

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[1] *Chem. News*, 19. 1, 1869.

[2] H. von Jüptner, *Journ. I.S. Inst.*, 49. 80, 1896; *Chem. News*, 74. 81, 1896; C. B. Dudley, *Journ. Amer. Chem. Soc.*, 15. 501, 1893; A. B. Prescot, *Chem. News*, 53. 78, 88, 1886; S. H. Collins, *Univ. Durham Phil. Soc.*, 1, 1909; E. A. Lewis, *Journ. Soc. Chem. Ind.*, 31. 96, 1912.

[3] H. Lundén, *Svensk. Kem. Tids.*, 24. 96, 1912.

[4] This explains some puzzling statements which confront the student who "consults the originals." Given three processes A, B, and C for a particular determination, the author of the process A may quote analyses to prove that A is superior to B and C; the author of B may try to prove that his process is superior to A or C; and similarly, the author of process C may set out to prove that C is superior to A and B.

of transfers from vessel to vessel, common sense will sometimes decide in favour of one of a number of rival processes. Other things being equal, *the "margin of safety," that is, the risk of error, is less the smaller the number of separations involved in isolating a given constituent.* The more complex the method of separation, the greater the influence of the personal factor. Other things being equal, *that method of analysis is safest which depends least on the skill of the operator.* In order to reduce the personal factor to a minimum in the determination of phosphorus and manganese in iron and steel, where accuracy *and* speed are of vital importance, and where the *general* composition and range of variation of the substances to be analysed are known, methods have been devised, chiefly by C. H. and N. D. Risdale,[1] for the rapid determination of the constituents just mentioned. These methods—styled *mechanicalised processes* and *analoid processes*—are followed "mechanically" with prescribed quantities of solvents, measured reagents, and ready-made tablets of solid reagents introduced at definite assigned temperatures, etc. In this way the trouble, expense, and uncertainty involved when differences occur in analyses made by different chemists are reduced to a minimum.

Proposals to *standardise processes of analysis* crop up from time to time. It is suggested that the methods of analysis in which manufacture and sale depend upon the results shall be standardised by an authoritative committee[2] and periodically revised. In this way, a greater uniformity in results might be expected. Progress would not necessarily be arrested, because improved methods would be examined by the committee periodically, and the less satisfactory methods cancelled.

(8) *Errors due to calculations based on different atomic weights.*—In this work we assume that the table of atomic weights indicated on page 684 is used. It may seem heresy to inquire if this is the best we can do. It will be obvious that the atomic weight question is of the greatest importance. It is not uncommon to find a difference of a few per cent. between the maximum and minimum values for the atomic weights found by different or by the same experimenters. The maximum value for the reliable determinations of the atomic weight of magnesium given by Clarke is 24·706; the minimum value 24·016.[3] In calculating the ratio $MgO : Mg_2P_2O_7$, page 221, we assumed the atomic weight of magnesium to be 24·32. It seems that under the ordinary conditions of chemical analysis, the weight may deviate at least (possibly more than) ± 0·3 from this value. This means that instead of taking the factor 0·362 for converting a given weight of magnesium pyrophosphate into magnesia, we require a factor somewhere between 0·3643 and 0·3603. With small amounts of magnesia, it does not matter which be used—0·36 will do quite well. With larger amounts of magnesia, the result may be affected by over one-fourth per cent. It might therefore be personally interesting for an analyst to find if he works under the 0·3643 or the 0·3603 conditions.

Many chemists recommend the use of an old discarded value for the atomic weight of platinum—197—in potash determinations for calculating the amount of KCl or K_2O equivalent to the K_2PtCl_6 precipitate.[4] There can be little doubt that the best chemists working with the best available instruments, under the best conditions, with the purest available materials, and with a few selected reactions, get a number nearer 195 than 197. Why then recommend 197? If, by a given analytical process, 197 gives a result nearer the correct value than 195, it is obvious that the former number should be employed in that process. It is, indeed, possible that if the atomic weight had been determined by the same reaction used in the analytical process, a number different from 195 would have been obtained. The conclusion is obvious. Each analytical process requires its own set of atomic factors, which may, or may not, coincide with the atomic weights given in the tables. Consequently, to get the best results in technical analyses, each chemist should find for himself the set of factors (or atomic weights) peculiar to that process.[1] If the ratio $K_2O : K_2PtCl_6$ under one set of conditions be 0·19308, and under another set of conditions 0·19384, it would be absurd to employ the former number for conditions where the latter number would have been obtained.

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[1] C. H. and N. D. Risdale, *Journ. I. S. Inst.*, **1.** 332, 1911; W. H. Herdsmann, *Journ. West Scot. I. S. Inst.*, 4, 1912.

[2] For discussions on the standardisation of analytical processes, see *Journ. Soc. Chem. Ind.*, **3.** 2, 210, 345, 356, 1884; J. Pattinson, *ib.*, **3.** 17, 1884; R. R. Tatlock, *ib.*, **3.** 307, 1884; J. C. Bell, *ib.*, **2.** 109, 1883; A. R. Ling, *ib.*, **22.** 677, 1903; C. Richardson, *ib.*, **20.** 334, 1901; J. White, *ib.*, **24.** 390, 1905; H. D. Richmond, *ib.*, **22.** 676, 1903; G. Lunge, *ib.*, *Chem. News*, **47.** 210, 1883; B. Blount, *ib.*, **86.** 177, 1900; H. von Jüptner, *ib.*, **74.** 81, 1896; *Journ. I. S. Inst.*, **49.** 80, 1896; W. D. Richardson, *Journ. Ind. Eng. Chem.*, **2.** 99, 1910. Page 248.

[3] F. W. Clarke, *A Recalculation of the Atomic Weights*, Washington, 222, 1910.

[4] F. Wolfbauer, *Chem. Ztg.*, **14.** 1246, 1890.

§ 117. The Statement of the Results.

It would be an advantage if different analysts adopted one uniform practice in stating their results, since analyses would then be much easier to read. The Fifth International Congress of Applied Chemistry at Berlin agreed that—

1. The name of the constituent is to be followed by the formula;
2. By the name of an acid, the acid itself and neither its anhydride nor its ion is to be understood; and
3. When the results are calculated in the form of metal oxide and acid anhydride, the latter is to be written either as "sulphuric anhydride, SO_3," or as "sulphuric acid (calculated as anhydride) SO_3."[2]

Washington and Hillebrand[3] recommend stating the results somewhat in the following order: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O (ignition), H_2O (below 110°), CO_2, TiO_2, ZrO_2, P_2O_5, SO_3, Cl, F, S, (FeS_2), Cr_2O_3, V_2O_3, MnO, NiO, CoO, CuO, ZnO, BaO, SrO, Li_2O, C, NH_3, and organic matter. The idea is to keep the important oxides at the head of the list, so that the general character of the silicate can be seen at a glance. This is no doubt excellent. For clays, I prefer to keep the titanium among the important constituents, since, in the higher grades of clay, it is often as important a constituent as iron, and more important than magnesia. The P_2O_5, SO_3, Cl, F, CO_2, and carbon are best kept as a separate group. For glazes, frits, etc., I also prefer to keep certain bases in a separate group. The following lists represent the order I use for commercial analyses of clays and glazes and similar materials, where the purpose of the analyses is different from that of Washington and Hillebrand:—

CLAY DRIED AT 109° C.	GLAZE DRIED AT 100° C.
Hygroscopic moisture lost at 109° C.	Hygroscopic moisture lost at 100° C.
Silica (SiO_2).	Silica (SiO_2).
Titanic oxide (TiO_2).	Alumina (Al_2O_3) and Ferric oxide (Fe_2O_3).[4]
Alumina (Al_2O_3).	Lime (CaO).
Ferric oxide (Fe_2O_3).	Magnesia (MgO).
Manganese oxide (MnO).	Potash (K_2O).

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[1] Or to the analyst himself.

[2] W. Fresenius. *Zeit. anal. Chem.*, 44. 32, 1905. See also *Chem. News*, 53. 186, 1886; E. C. C. Stanford, 16. 29, 190, 1874; C. G. Hopkins, *Journ. Amer. Chem. Soc.*, 29. 1312, 1907.

[3] H. S. Washington, *Amer. J. Science* (4), 10. 59, 1900; *Prof. Paper U.S. Geol. Sur.*, 14. 24, 1903; 28. 7, 1904; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 305. 27, 1907.

[4] There is usually no need to separate the constituents of the ammonia precipitate unless phosphates be present.

CLAY DRIED AT 109° C.

Magnesia (MgO).
Lime (CaO).
Potash (K_2O).
Soda (Na_2O).
Loss when calcined over 109° C.

Chlorine (Cl).
Fluorine (F).
Phosphoric oxide (P_2O_5).
Sulphur (S).
Sulphur trioxide (SO_3).
Carbon (C).
Carbon dioxide (CO_2).

GLAZE DRIED AT 100° C.

Soda (Na_2O).
Loss when calcined over 100° C.[1]

Lead oxide (PbO).
Tin oxide (SnO_2).
Zinc oxide (ZnO).
Barium oxide (BaO).

Fluorine (F).
Phosphoric oxide (P_2O_5).
Sulphur trioxide (SO_3).
Carbon dioxide (CO_2).
Boric oxide (B_2O_3).

If there is any evidence showing the way the acids and bases are combined, the amounts may be stated separately—*e.g.*, calcium carbonate (whiting), white lead, calcium fluoride, etc. When the way the acids and bases are combined is open to doubt, it is best to leave the adjustment to those who intend to transform the analysis of, say, a glaze into a recipe, etc.[2]

It is sometimes difficult to decide how best to report the separate constituents in an analysis, since curious practices prevail in buying and selling which are not always those most convenient for the consumer. Manganese ores, for instance, may be sold on their per cent. of metallic manganese, or manganese peroxide; cerium is weighed as cerium dioxide, but the earths are sold on their per cent. Ce_2O_3; chromium ores are valued on their Cr_2O_3 contents; tungsten ores on their WO_3 contents; tantalum and vanadium ores on the amount of the respective elements equivalent to Ta_2O_5 and V_2O_5 they contain; while uranium ores are valued on their equivalent U_3O_8.[3] Analysts must then bow to the inexorable fetish—custom.

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[1] The interpretation of "loss on ignition" is somewhat indefinite with glazes, and is rather a qualitative indication of the character of the glaze in question.

[2] For an example of the discrepancies which may arise when the analyst attempts to go beyond his facts, and show the mode in which the "bases" and "acids" are combined, compare H. M. Noad, *Journ. Chem. Soc.*, **14**. 43, 1862; and A. Voelcker, *ib.*, **14**. 46, 1862; *Chem. News*, **3**. 77, 285, 315, 1861.

[3] G. T. Holloway, *Trans. Inst. Min. Met.*, **21**. 569, 1912.

CHAPTER XIX

ELECTRO-ANALYSIS

§ 118. Some Definitions.

If two platinum plates be dipped in an aqueous solution of, say, copper sulphate, and the plates be connected by wire with the poles of a battery or accumulator, metallic copper will be precipitated on one plate, and if the conditions be suitable, practically all the copper will separate in the form of a compact coherent metallic film. If the plate with the film of copper be washed, dried, and weighed, the increase in the weight of the plate—before and after the experiment—will represent the amount of copper which was present in the solution under investigation.

The process of decomposition is called *electrolysis*; the solution undergoing decomposition is called an *electrolyte*; the two plates by which the current enters and leaves the electrolyte are called *electrodes*. The electrode by which the current is conventionally supposed to enter the electrolyte is called the *anode*; and the other electrode is called the *cathode*.[1]

What has just been stated about the solution of copper sulphate applies to many other metallic salts. When such solutions are electrolysed, the metal is deposited on the cathode. But with solutions of lead and manganese salts, the peroxides are sometimes deposited on the anode. In applying these facts to practical analysis, it is convenient to make the dish holding the electrolyte one of the electrodes—generally the cathode—on which the deposit is to be collected.

The quantity of electricity which passes through the solution in unit time, or the speed of the current, is measured by an *ammeter*. The unit is called an *ampere*.[2] The unit of the electric pressure[3] driving the electric current along the circuit is called the *volt*,[4] and the voltage of the current is measured by the *voltmeter*. The current is regulated by coils of wire, incandescent lamps, etc., which obstruct the steady flow of the current of electricity and fritter the energy of the electric current down into heat. The unit of resistance is called the *ohm*.[5]

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[1] It is always easy to determine which wire from the battery or accumulator belongs to the cathode, and which to the anode, by wetting a piece of blotting paper with an aqueous solution of potassium iodide and starch, and allowing the tips of the two wires to touch the wet paper about a quarter of an inch apart. The paper in the vicinity of the wire to be attached to the anode will be coloured blue. If the blotting paper be soaked in a solution of sodium chloride and phenolphthalein, the paper in the vicinity of the cathode will be coloured red. Paper prepared in this way is called "pole paper," and is sold in booklets or rolls like litmus paper.

[2] The ampere "is represented by the unvarying electric current which, when passed through a solution of silver nitrate in water, deposits metallic silver at the rate of 0·001118 grm. per second."

[3] Also called the electromotive force, or potential.

[4] The volt "is represented by the electrical pressure that if steadily applied to a conductor whose resistance is one ohm will produce a current of one ampere."

[5] The ohm is the unit of resistance and "is represented by the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice 14·4521 grms. in mass, of a constant sectional area and a length of 106·3 cm."

There is an interesting relation—*Ohm's law*—between these magnitudes:

$$\text{Quantity of electricity (amps.)} = \frac{\text{Pressure (volts)}}{\text{Resistance (ohms)}}.$$

Consequently, decreasing the resistance opposed to, or increasing the voltage of a current will increase the quantity of electricity passing through a circuit per second (amperage); and, conversely, increasing the resistance or decreasing the voltage will decrease the quantity of electricity passing through the circuit per second.[1]

§ 119. Some Factors which determine Success in Electro-analysis.

1. *Pressure of the Current—Decomposition Voltage.*—For the decomposition of every metallic solution, the pressure of the electric current must exceed a certain minimum value. This minimum voltage is characteristic of the particular solution under investigation. For instance—

Sulphates.	volts.
Nickel sulphate	2·09
Cadmium sulphate	2·03
Cobalt sulphate	1·92

Chlorides.	volts.
Nickel chloride	1·85
Cadmium chloride	1·88
Cobalt chloride	1·78

A current of many amperes might be passed through a solution of cobalt sulphate without any visible decomposition; only when the voltage exceeds 1·92 volts will cobalt be deposited. If a solution contains a mixture of salts of different metals, the electrodes appear as if they exerted a kind of selective action which really depends upon the minimum voltage required to effect the decomposition of the different metallic salts. This peculiarity of the salts can be employed to effect the separation of the different metals. In a solution containing zinc and cobalt sulphates, for example, cobalt will be deposited with a voltage less than 2·02 volts, and greater than 1·92 volts. When all the cobalt is deposited, increasing the voltage above 2·08 volts will lead to the deposition of zinc.

2. *Strength of the Current—Current Density.*—The weight of a given metal deposited by a current of electricity is proportional to the quantity of electricity (amperes) passing through the solution; and the weights of different metals deposited by the same quantity of electricity (amperes) is directly proportional to the chemical equivalents of the metals in the solutions (Faraday's laws). Thus, a given quantity of electricity will deposit the relative quantities of the different metals indicated in the last line of the following scheme:—

	Al	Ni	Co	Sn(ic)	Cu	Cd
Atomic weight	27·1	58·68	58·97	119·0	63·57	112·4
Chemical equivalent	9 03	29·34	29·48	29·75	31·78	56·2

The quantity of metal deposited in a given time, that is, the rate of deposition, is dependent upon the strength of the current in amperes. The deposited metal redissolves in the electrolyte, and, consequently, the rate at which the metal is deposited must exceed the rate at which it redissolves. The metal is only deposited from the solution in the immediate vicinity of the cathode. Hence, other things being equal, the greater the area of the cathode the more metal available for deposition, and, *mutatis mutandis*, the greater the rate at which the metal is redissolved. Hence, the amount of current necessary to deposit the metal will depend upon the area of the cathode.

The amount of current per unit area (per second) is called the *current density*—100 sq. cm., that is, 1 sq. decimetre, is generally taken as unit area. Hence, "a current density of 2 amperes" means that 2 amperes should be used for each 100 sq. cm. of cathode area.

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[1] J. W. Richards, *Chem. News*, **94.** 5, 20, 31, 1906—"Electrochemical Calculations."

While the tendency of a metal to redissolve in the solution fixes a lower limit to the amount of current which may be used for electro-analysis, the tendency of the metal to form spongy, non-adherent films when deposited too rapidly prevents the use of currents exceeding a certain maximum strength (amperage per unit area of cathode).

It is highly important, for accurate work, to precipitate the metal in a coherent film which is easily washed and weighed. The condition of the deposited metal is not only dependent upon the voltage and the current density, but is also determined by the nature of the solution from which the metal is deposited, the amount of free acid, the temperature, etc. These "optimum" conditions can only be determined by trial and failure.

3. *Nature and Concentration of Electrolytes.*—Enough salt should be present in the solution to carry the current, otherwise hydrogen, or some other element, may cause the film of metal to become spongy and impure. The more concentrated the solution, the greater the amount of metal in solution in the neighbourhood of the cathode. The nature of the salt undergoing decomposition is of importance. Copper nitrate, for example, gives better results than copper sulphate; and nickel sulphate is far more satisfactory than nickel nitrate. Better deposits are frequently obtained with complex salts like the metallo-cyanides, double oxalates, etc., than with the simple sulphates, nitrates, etc.

4. *Nature and Concentration of Foreign Salts in the Electrolyte.*—A current density which gives a perfectly pure coherent deposit of, say, copper when no other metal is present may give a very impure deposit when, say, arsenic is present, particularly if the decomposition voltage of the foreign salt be near that of the copper salt. The greater the concentration of the foreign salt, the greater the danger of its simultaneous deposition with the copper.

5. *Temperature.*—The time required for the complete electrolysis of certain solutions, *e.g.*, copper or nickel sulphate, lead nitrate, etc., is frequently abbreviated by working at a higher temperature, but the deposits are not always so good as those formed at lower temperatures. When working at an elevated temperature, care must be taken not to heat the solution to its boiling point, or the deposit may be loosened from the cathode, and an accurate determination is then impracticable.

6. *Condition of the Electrolyte.*—Only those metallic salts in the vicinity of the electrodes can be decomposed by the current, and the diffusion of more salt from the body of the solution to the vicinity of the electrodes is comparatively slow. Hence, adequate agitation of the solution will greatly accelerate the speed of precipitation by supplying fresh metal to take the place of the metal withdrawn from the solution faster than it can be supplied by simple diffusion. When artificial means are used to agitate the solution during electrolysis, a greater maximum current density can be used. Only one of the electrodes is usually rotated, and the consequence is that the current may be considerably increased without injuring the deposit; and deposits which require several hours under ordinary conditions may be completed in as many minutes. This subject will be discussed later.

In giving directions for electrolytic separations, or in stating the results of experiments, the following factors, apart from those connected with the apparatus, are to be considered essential for success:—

1. Pressure of electric current in volts.
2. Current density in amperes per square decimetre.
3. Nature and concentration of the electrolyte.
4. Nature and concentration of foreign salts dissolved in the electrolyte.
5. Temperature of the electrolyte.
6. Condition of the electrolyte—at rest, or agitated.

If attention be paid to these details necessary for successful work, many electrolytic methods of analysis rival in accuracy, neatness, and rapidity the best of the gravimetric and volumetric processes available for the same metal. In consequence, a number of electrolytic methods have won a permanent place in analytical chemistry. True enough, the time required for the electrolysis is prolonged, but very little attention is needed during the actual electrolysis. Indeed, many electrolyses can be safely left 12 hours—say overnight—without attention. Those methods involving the use of rotating electrodes enable a determination to be made in 10 or 15 minutes. An example is given on page 337.

§ 120. The Apparatus for Electro-Analysis.

When a relatively small number of determinations is made, the outfit will be different from that employed when determinations are frequently practised. The former will alone be considered here. For the latter, special text-books[1] must be consulted. The determination of copper is conveniently taken as a standard process for reference. This is also particularly appropriate not only because of the typical character of the process, but also because the Mansfield Oberberg und Hüttendirection, in 1867, offered a prize for a rapid and accurate method for the determination of copper in ores. The prize was won by C. Luckow[2] for an electrolytic process. This gave an impetus to electro-analysis generally.

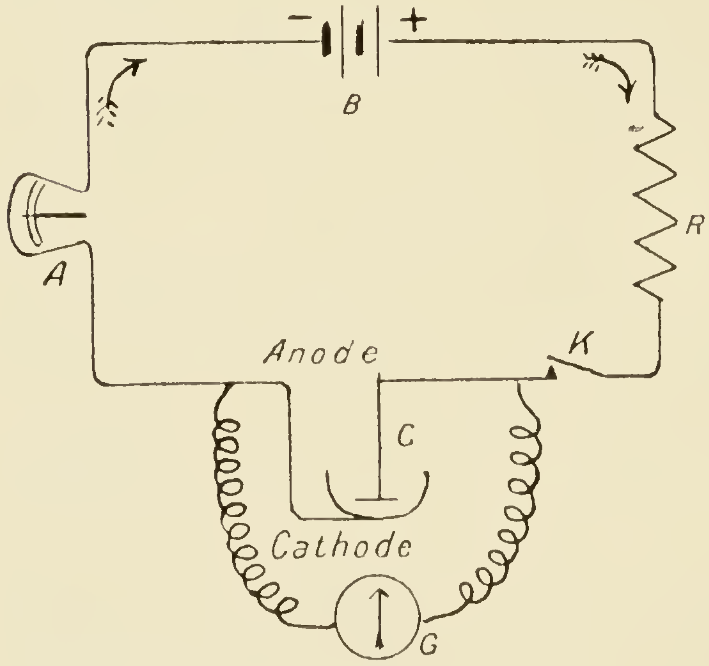

Fig. 117.—Plan of fig. 118.

A plan of the outfit for occasional work is shown in fig. 117. The current from an accumulator *B* passes through the resistance *R* to the decomposition cell *C*, then through the ammeter *A*, and back to the accumulator. A voltmeter *G* is placed in metallic contact with the cathode and anode. Usually a couple of 2-volt E.P.S. accumulator cells *B* will suffice for the current. The key K is for making or breaking the passage of the current as desired.

A photograph of the apparatus is shown in fig. 118. The electrolytic cell shown at *C* is the type recommended by Classen. It consists of a platinum basin, about 200 c.c., with or without an inner matted surface.[3] This serves as the electrode for collecting the deposit. A perforated platinum disc fixed to a stout platinum wire may be used for the other electrode.[1] The dish rests on a brass "retort ring" to which three platinum points have been fixed to ensure electrical contact between the retort ring and the platinum dish. The ring is clamped to a glass rod fixed to a heavy iron base. The platinum wire supporting the disc is also fixed by a suitable clamp to the same glass rod. The glass rod serves to insulate the disc from the dish. If otherwise, the current would "short circuit" and not pass through the decomposition cell. Binding screws are fixed to the clamps, so that the dish and disc can be put into electrical contact with the battery.[2]

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[1] A. Classen, *Quantitative Analyse durch Electrolyse*, Berlin, 1908 ; B. B. Boltwood's trans., New York, 1908 ; A. Fischer, *Electroanalytische Schnellmethoden*, Stuttgart, 1908 ; F. M. Perkin, *Practical Methods of Electro-chemistry*, London, 1905 ; J. Riban, *Traité d'analyse Chimique Quantitative par Électrolyse*, Paris, 1899 ; B. Hollard and L. Bertiaux, *Analyse des Métaux par Électrolyse*, Paris, 1909 ; E. F. Smith, *Electro-analysis*, Philadelphia, 1907 ; B. Neumann, *Theorie und Praxis der analytischen Elektrolyse der Metalle*, Halle a. S., 1897 ; J. B. C. Kershaw's trans., London, 1898.

[2] C. Luckow, *Zeit. anal. Chem.*, 8. 23, 1869 ; 19. 1, 1880.

[3] The nature of the surface of the electrodes is of importance. Some metals give less satisfactory deposits on hammered surfaces than on spun and polished surfaces. In the determination of lead as peroxide, the precipitate only adheres firmly to the electrode when the surface has been roughened by means of, say, a sand-blast. A woven platinum gauze electrode—flag electrode—is also recommended in special cases. The electrode must be quite clean, or a poor deposit will be obtained.

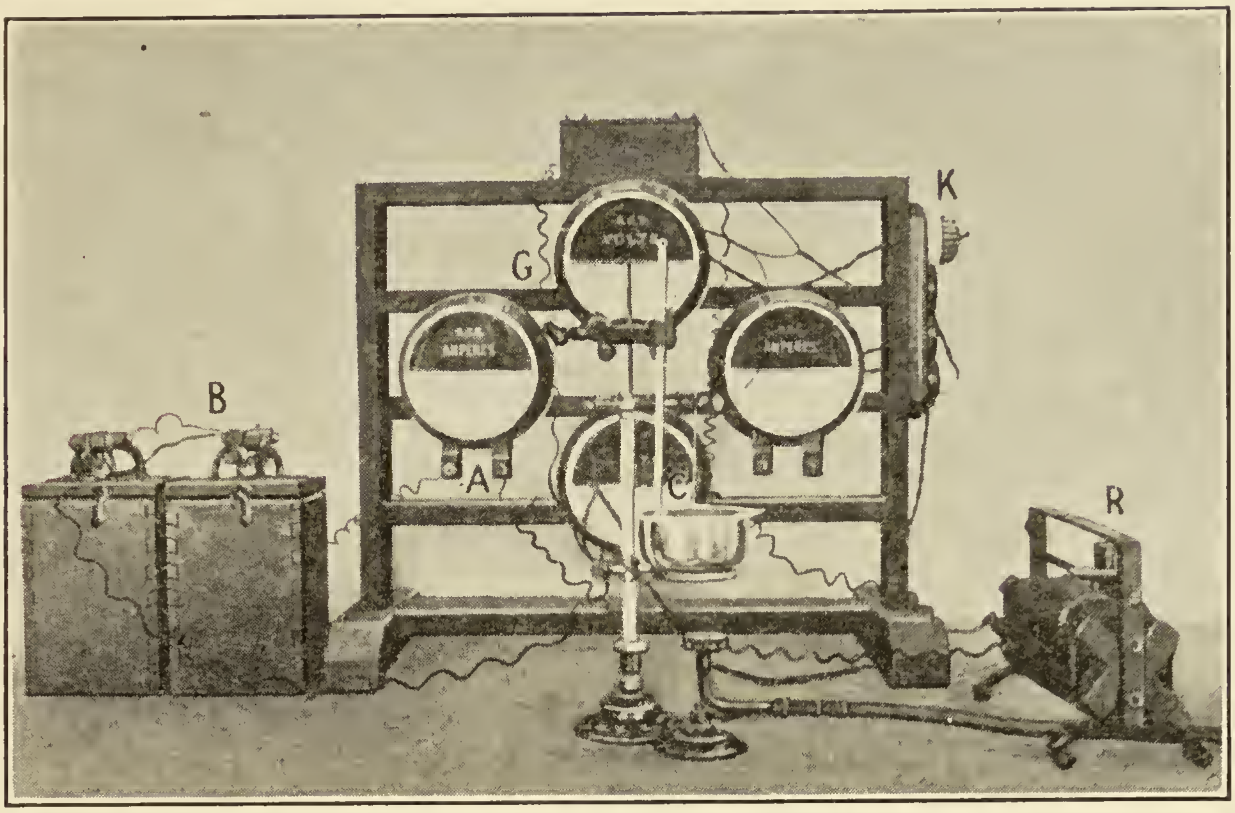

FIG. 118.—The apparatus for an electro-analysis (electrodes stationary).

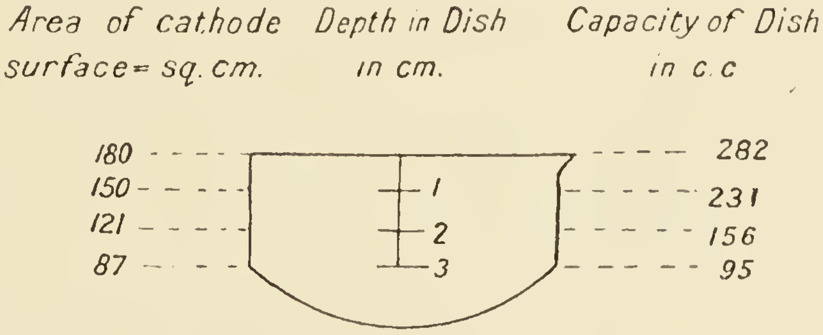

FIG. 119.—Classen's dish.

Classen's dish, shown in fig. 119, is 9 cm. in diameter, and 4·2 cm. deep. It holds about 250 c.c., and weighs between 35 and 37 grms. The dish shown in the diagram held 231 c.c. when filled to within 1 cm. of the upper edge; and 156 c.c. when filled to within 2 cm. of the upper edge. With a disc anode, the best distribution of the current is obtained by adjusting the disc so that it is exactly in the centre of the dish and about 2 or 3 cm. below the upper edge.

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[1] Several other types of anode and cathode are in use—dishes, cones, cylinders, gauzes, spiral wires, etc. The important points about the electrodes are: (1) they must not be attacked by the electrolyte, nor absorb gas; (2) they must be of such a shape that the density of the current on the electrode which receives the deposit is as homogeneous as possible; and (3) the shape must favour rapid diffusion of the electrolyte from one electrode to the other.

[2] It is easy to make less expensive supports than the one here described. A lot depends upon the "taste" of the worker. The construction of apparatus for electrolytic work lends itself to what Ostwald calls "Basteln"—pottering. The voltmeter and ammeter stand in the background of fig. 118 has ammeters and voltmeters for running two independent determinations at the same time.

If the electrolytic cell is to be heated, a thin asbestos board or quartz plate is placed under the dish, and the vessel is heated by a small burner (fig. 118) so as to ensure a uniform temperature.

The resistance or rheostat *R*, shown in the photograph, is made from platinoid wire wound on an asbestos-covered brass tube, or on a slate frame. By moving the sliding contact along a bar, any desired resistance can be obtained within the capacity of the instrument.[1]

The ammeter *A* is an instrument with a small internal resistance—so small that it can, for most purposes, be neglected. In consequence, the ammeter is kept in the main circuit all the time an experiment is in progress. A 20-amp. meter reading to $\frac{1}{10}$ amp. will suffice for the work described in this book.[2]

The voltmeter *G* has a relatively large internal resistance, and if placed in the main circuit would oppose so much resistance to the passage of the current that very little current would pass at all, or the coils of the voltmeter would be burnt out. If, for instance, the voltmeter has a resistance of 1000 ohms, and the electrolytic cell 2 ohms, the ratio of the current passing through the decomposition cell to that passing through the voltmeter will be as 500 : 1. The voltmeter may be left in the "shunted" circuit all the time an electrolysis is in progress. A voltmeter reading 0 to 20 volts graduated in half-volts is sufficient.[3]

§ 121. The Electrolytic Determination of Copper.

Copper can be satisfactorily deposited from solutions acidified with nitric or sulphuric acids, but not hydrochloric acid, except under special conditions. Nitric acid gives better results than sulphuric acid. The determination will be here described in some detail to serve as a type for later references.[4]

1. *Cleaning the Electrodes.*—The electrodes must be perfectly clean. Never touch the depositing surfaces of the electrodes with the fingers, to avoid danger of contaminating the surfaces with grease. Clean electrodes are absolutely necessary for good deposits. Silver soap or round-grained sea sand applied with a soft cloth or small sponge is commonly used for scouring and polishing. Grease is removed either by heating the electrodes to redness,[5] or by immersion in a saturated solution of chromic acid (or potassium dichromate) in concentrated sulphuric acid. Wash with distilled water, and dry by warming. The cathode is cooled in a desiccator, and weighed.

2. *Preparation of the Electrolyte.*—Dissolve a gram of copper sulphate in 140 c.c. of distilled water; add 5 to 10 c.c. of nitric acid (sp. gr. 1·42), so as to make the solution between 8 and 10 per cent. nitric acid. The solution is placed in the weighed platinum dish. If the electrolysis is to be conducted at an elevated temperature, say 60°, warm the solution in the dish, and adjust the gas so as to maintain the necessary temperature.[6]

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[1] Numerous other types are used. Some of these will be found described in the text-books cited above.

[2] Ammeters with a range 0–2 amps. reading in hundredths, provided with a shunt for reading 0–20 amps. in tenths, will be ample for other work than that described here.

[3] In purchasing a new instrument, one reading 0–3 volts in tenths, provided with a shunt for reading 0–30 in half-volts, will be found useful for work with rotative electrodes.

[4] W. C. Blasdale and W. Cruess, *Journ. Amer. Chem. Soc.*, 32. 1231, 1910; D. J. Demorest, *Journ. Ind. Eng. Chem.*, 5. 216, 1913.

[5] Never heat platinum electrodes unless every particle of the previous deposit has been removed, otherwise an alloy may be formed which will spoil the apparatus. See page 114.

[6] If the solution contained much free nitric acid, it should be evaporated to dryness, and the residue dissolved in the prescribed amount of nitric acid and water. If the solution contained much free sulphuric acid, the solution should be neutralised with ammonia, and the necessary amount of nitric acid added.

3. *Adjustment of the Apparatus.*—The apparatus is fitted up as indicated in fig. 118. See that all the metallic contacts—battery connections, connections with the voltmeter, ammeter, resistance, and electrolytic stand—are clean and rigid. If otherwise, the contacts may, later on, offer so much resistance that the current is either weakened or interrupted. The anode should be adjusted in the centre of the dish, and at a sufficient distance (0·5 to 1 cm.) from the cathode to present sufficient resistance to prevent the necessity of using a very high voltage when the current has started. It is best to arrange the resistance, etc., so that when the circuit is closed a current no greater than the maximum required passes through the circuit. Cover the platinum dish with a watch-glass cut in two pieces, and provided with notches for the anode, and also for a thermometer if the electrolysis is to be conducted at an elevated temperature. The watch-glass is intended to prevent loss by the spray carried off with the gases liberated at the anode.

4. *The Electrolysis.*—Complete the circuit and adjust the resistance so that a current of from 2·0 to 2·5 volts[1] passes through the circuit, and a current density of 0·5 to 1·0[2] amp.[3] A bright red film will flash over the cathode surface as soon as the circuit is closed. The electrolysis will be finished in about 4 hours.

If the electrolysis is to run overnight, a current density of about 0·1 amp. will suffice. A little more nitric acid—2 c.c.—should also be added, since some of the nitric acid is converted into ammonia by the hydrogen liberated at the cathode, and this is inclined to cause a spongy deposit.

To find if all the copper has been deposited, raise the level of the solution by the addition of a few c.c. of distilled water. If no copper is deposited on the newly exposed cathode surface after a run of about 15 minutes, it may be assumed that the electrolysis is finished.[4] Or, a few drops of the electrolyte may be transferred by means of a pipette to a test-tube, and test for copper in the ordinary manner, say, make alkaline with ammonia, then acidify with acetic acid, and add a few drops of potassium ferrocyanide. A brownish-red precipitate shows that all the copper has not been deposited, and that it is necessary to continue the electrolysis. When no coloration appears on repeating the test, the electrolysis is completed.

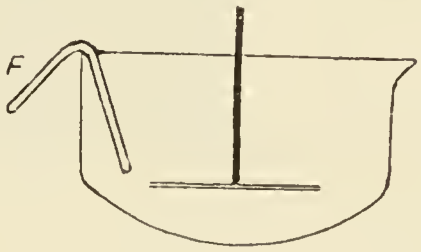

FIG. 120.

5. *Washing and Drying the Deposited Metal.*—Since the precipitation has been made in an acid solution, some consider that the current should not be stopped until the acid liquid has been removed, otherwise the dissolution of the deposited copper will start before the plates can be washed, and thus lead to low results. In most cases, however, sufficiently accurate results will be obtained by breaking the current, and immediately[5] pouring the solution into

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[1] The voltage and current density depend upon the resistance of the electrolytic cell, which in turn depends upon the conductivity of the solution, the size and shape of the electrodes, and the distance apart of the electrodes. It is frequently inconvenient to regulate these two factors to correspond exactly with prescribed directions. In that case, bring the voltage to the desired value, and let the current adjust itself to the required amperage. This is particularly the case with separations where the decomposition voltage is of prime importance.

[2] If other metals are present in the solution, keep to the lower amperage.

[3] From fig. 119 we see that the dish with 150 c.c. of solution offers a cathode surface of approximately 120 sq. cm. Hence, if 0·8 amp. is needed per 100 sq. cm., a cathode surface of 120 sq. cm. will require a current of 1 amp. read on the ammeter.

[4] Classen (*l.c.*) places a small strip of bright platinum foil in contact with the cathode (*F*, fig. 120), but not touching the anode. If after half an hour no deposit is formed on the foil immersed in the liquid, it is safe to assume that the electrolysis is complete.

[5] F. Rüdorff (*Zeit. angew. Chem.*, 6. 5, 1892) adds 10 drops of a saturated solution of sodium acetate just before breaking the circuit. The acetic acid which is set free does not attack the

an empty beaker, and rapidly rinsing out the basin with hot distilled water. Finally, wash three times with about 5 c.c. of alcohol,[1] and once with ether.[2] Dry the precipitated copper in an air-bath at about 80°; cool in a desiccator, and weigh.

When it is desired to wash the deposit free from acid before stopping the current—the acid liquid is syphoned off (by suction) into a filtration flask, and at the same time fresh distilled water is poured into the basin until the washings are free from acid before stopping the current. A method of doing this is illustrated in fig. 121. Then wash the deposit with hot distilled water, etc., as indicated above.

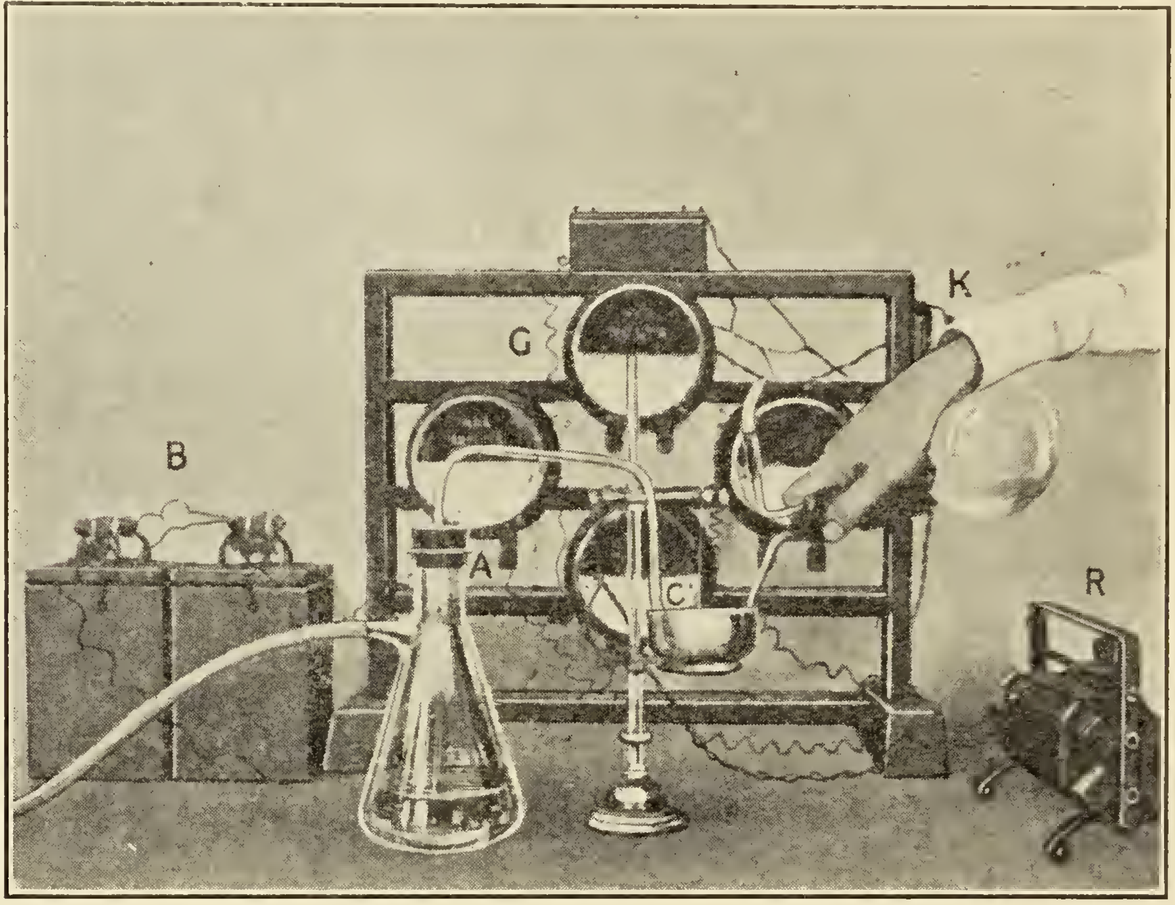

Fig. 121.—Washing the cathode dish.

6. *Errors.*—If the current density be too high, the deposit may be "burnt." In that case, the copper, instead of appearing as a bright red coherent film, is coloured more or less brown, and appears more or less pulverulent and non-adherent. If the current be acting for too long a time, there is a possibility of some of the sulphuric acid being reduced by the hydrogen liberated at the cathode to form hydrogen sulphide. In that case, some copper sulphide will be formed, and this leads to the development of dark brown spots on the copper.

If arsenic or antimony be present, these elements may be deposited with the copper, giving it a dull and maybe a grey appearance. In that case, the

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copper immediately, and in consequence there is sufficient time to wash the plates before appreciable action has occurred.

[1] The alcohol should give no residue on evaporation to dryness. The alcohol should also have been distilled over lime. Instead of absolute alcohol, methylated spirit free from mineral oil can be used. The methylated spirit is purified by standing in contact with caustic soda for a few days, and distilling. Freshly burnt lime is now added to the distillate, and after standing 24 hours, the spirit is decanted into a distilling flask containing some freshly burnt lime, and redistilled.

[2] The ether is supposed to have been distilled over caustic potash. Some omit the ether treatment.

copper deposit may be heated to dull redness to volatilise the oxides of arsenic and antimony.[1] Dissolve the resulting copper oxide in nitric acid, and repeat the electrolysis. Hollard and Bertiaux say that the addition of a little ferric sulphate lessens the danger of precipitating arsenic; and the addition of a little lead nitrate, the deposition of antimony. If much arsenic, antimony, or bismuth be present, they should be separated chemically before the electrolysis.

Silver, if present, will be deposited with the copper, and should therefore be removed from the solution before the electrolysis, or the metal deposited on the cathode can be weighed as "silver + copper." The mixed metals are then dissolved in nitric acid, and the silver determined by the addition of a little hydrochloric acid in the usual manner. Tin and mercury, if present, may also be deposited with the copper.

In illustration of the results which may be obtained with the process just described:—

Used	25·08	25·08	25·08	25·08	per cent.
Found	25·08	25·05	25·07	25·04	,,

7. *Recording the Results.*—The results entered in the note-book will include the following data:—

1. Current pressure: 2·2–2·5 volts.
2. Current density: 0·5 amps.
3. Electrolyte: 1 grm. of copper sulphate with 8 to 10 per cent. of nitric acid, made up to 150 c.c.
4. Foreign salts: no foreign metallic salts were present.
5. Temperature: 15°–20°.
6. Electrodes: stationary.

Time, 4½ hours.

One gram of the sample was dissolved as indicated on page 258, and used as the electrolyte. The weighings were:—

Cathode and deposit	36·3542 grms.
Cathode	36·0734 ,,
Copper deposit	0·2808 grm.

Hence, the sample contained 28·08 per cent. metallic copper.

8. *Cleaning the Deposit from the Electrode.*—In the case of copper, the deposit can be readily removed from the platinum dish by the action of dilute nitric acid, and subsequent washing with distilled water.

Electrolysis of Sulphuric Acid Solutions.—It may be desirable to precipitate the copper from a sulphuric acid solution free from nitric acid. The deposits of copper are not then quite so red in colour as when nitric acid is present. Between 7 and 10 per cent. H_2SO_4 is added, that is, about 4 c.c. per 100 c.c. of solution. According to C. Engels, the deposits are better if from 1 to 1½ grms. of hydroxylamine sulphate be present.[2] About 2·5 volts and a current density of 0·5 amp. are employed. The best temperature is from 70° to 80°. Between 1 and 1½ hours are needed for the electrolysis. The process is used when copper is to be separated from zinc, cadmium, nickel, and less than 0·1 grm. of iron. If over this amount of iron—say, up to 0·6 grm.—be present, the electrolysis must be conducted at atmospheric temperatures.[3] The time required for the electrolysis is then between 2 and 2½ hours. For an overnight electrolysis, use rather less sulphuric acid, and 0·5 grm. of hydroxylamine sulphate, also a current density of about 0·1 amp.

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[1] Remember that a platinum dish will not stand much of this sort of treatment.

[2] A. Classen recommends urea for the same purpose. In that case, some carbon is deposited with the copper, and the subsequent correction is troublesome.

[3] O. Foerster, *Zeit. angew. Chem.*, **19**. 1890, 1906.

Electrolysis of Ammoniacal Solutions.—Add ammonia to a solution of copper chloride containing less than 2 grms. of copper. When the precipitate has redissolved, add 20–25 c.c. of ammonia (sp. gr. 0·96) for quantities of copper up to 0·5 grm., and 30–35 c.c. for quantities up to 1 grm. Add 3–4 grms. of ammonium nitrate. If up to 0·5 grm. of copper be present, use a current density of 0·5 amp., and so proportionally up to 2 amps. for 2 grms. of copper. Time: about 2 hours. If insufficient ammonia be present, a brown non-adherent deposit collects on the anode, which falls off and contaminates the cathode deposit.[1]

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[1] F. Oettel, *Chem. Ztg.*, **18.** 47, 879, 1894; F. Rüdorff, *Ber.*, **21.** 3050, 1888.

PART III.

ANALYSIS OF GLASSES, GLAZES, COLOURS, AND COMPLEX SILICATES.

CHAPTER XX.

THE ANALYSIS OF GLAZES, GLASSES, ENAMELS, AND COLOURS.

§ 122. The Selection of the Sample.

The glaze to be analysed may be—partly or wholly—raw or fritted.[1] In the latter case, the method of analysis is the same as for glasses, enamels, and frits. Again, if a fired glaze be in question, it is usually necessary to chip the glaze from the body with a chisel and hammer. In that case, it is impossible to prevent part of the body being analysed with the glaze, because (1) the glaze while being fired dissolves some of the constituents of the body; and (2) the mechanical separation of chippings of the glaze from the body, even under a good lens, is laborious and unsatisfactory.[2] In the case of iron enamels, the analysis will include part of the intermediate flux between the enamel and the metal.[3] To remove a glaze or enamel from a body, de Luynes[4] recommends roughening the surface of the glaze with emery or carborundum paper or a file, and coating the roughened surface with wet glue. The glue is dried and baked in an air-bath. During the drying, the glue sometimes drags part of the glaze or enamel from the body. The glue can be removed by means of boiling water, and washing the fragments on a filter paper.

As a rule glazes contain silica, boric oxide, alumina, ferric oxide, lime, magnesia, lead oxide, and alkalies.[5] There may also be present tin oxide, baryta, phosphoric and sulphuric oxides, and fluorine. In special cases, zirconia, antimony, and arsenic may be present. In the case of colours, zinc, chromium, cobalt, nickel, manganese, copper, bismuth, cadmium, titanium, uranium, molybdenum, and gold may be found. The last six elements named are rare.[6] Selenium is occasionally found in clear glasses and frits. The general scheme for the separation of the more common elements is as follows:—

I. *Hydrogen sulphide group.*
   (1) *Copper group.*—Insoluble in sodium sulphide—*e.g.*, copper, lead, bismuth, cadmium.
   (2) *Arsenic group.*—Soluble in sodium sulphide—*e.g.*, arsenic, antimony, tin.

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[1] An examination of the constituents removed by treatment with dilute acids, and the determination of the carbon dioxide and water, will often furnish valuable data for reconstructing such glazes from the analysis.

[2] The interpretation of the analysis is then more or less obscure and vague.

[3] Fragments of iron may be removed with a magnet.

[4] V. de Luynes, *Comp. Rend.*, 134. 480, 1902.

[5] Along with carbon dioxide and combined water with raw and partially fritted glazes.

[6] Molybdenum, gold, silver, iridium, rhodium, and platinum are extremely rare. Tungsten is rare, although traces are common enough in tin glazes. It is introduced as an impurity with the tin oxide, and its presence is not always objectionable.

II. *Ammonia group*, or basic acetate group—*e.g.*, aluminium, iron, titanium, chromium.

III. *Ammonium sulphide group—e.g.*, zinc, manganese, cobalt, nickel.

The treatment when the rarer elements are present is discussed later. The boric oxide is determined on a separate sample by the methods described later. We first discuss the metals precipitated by hydrogen sulphide in acid solutions; and follow by a discussion of the processes required when zirconium, manganese, uranium, cobalt, nickel, chromium, zinc, etc., are present. In any case, the given sample is ground to a fine powder (page 121).

§ 123. "Opening" the Sample.

The method to be employed for the analysis of a glaze is determined by the result of the qualitative analysis. The colour of the glaze, etc., is often a good indication of the colouring oxides present. If the glaze contains unfritted white or red lead, a preliminary digestion with dilute acetic, hot hydrochloric, or nitric acid will remove the lead. The insoluble residue is fused[1] with sodium carbonate (as indicated page 164), and the fused mass digested with, say, dilute nitric acid. The solution may be added to that obtained by the preliminary digestion with nitric acid.

If all or part of the lead be fritted, and the frit is not completely decomposed by digestion with these acids,[2] another procedure must be followed. The lead frit can be fused in a platinum crucible provided there be no possibility of reducing conditions developing in the interior of the crucible. If tin oxide be present, it will dissolve in the molten sodium carbonate slowly.

Fusion with Sodium Hydroxide or Peroxide.—An enamel, glaze, or glass containing antimony,[3] arsenic, or tin oxide can sometimes be conveniently fused with eight to ten times its weight of sodium hydroxide[4] (or sodium peroxide) in a silver or nickel crucible at a dull red heat until the mass is fused. Dissolve the fused mass, when cold, in a little water or dilute hydrochloric acid. The objection to the use of caustic alkalies is their tendency to froth over, and the time necessary for the solution of the powder.[5] The following is the best way of conducting the operation:—The crucible[6] is placed in a circular hole cut in a sheet of $\frac{1}{8}''$ asbestos millboard, so that the crucible when pressed tightly into the aperture projects on the upper side about a quarter of an inch. The lid of the crucible is tapped on an agate mortar with a round-faced hammer, so that the lid fits the crucible with its convex side downwards. Any portions projected from the melting mass on the under side of the lid travel to the centre of the lid, and drop back into the crucible. A single Bunsen's burner will heat a small charge to a dull red heat. This usually suffices for the decomposition. The mouth of the crucible is kept cool, and the fused salt does not creep over the edges of the crucible. The results are usually excellent. A similar remark applies to the fusion with sodium peroxide as described for chromite,[1] page 474.

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[1] Care must be taken in using a platinum crucible when metallic oxides and salts are present, or the crucible may be attacked during the sodium carbonate fusion, etc.

[2] For the joint effect of acids and a metal like zinc, see T. Moore, *Chem. News*, **67**. 267, 1893.

[3] For the volatilisation of antimony during the fusion with sodium carbonate, see H. N. Warren, *Chem. News*, **67**. 16, 1893.

[4] A "pinch" of powdered wood charcoal—quarter gram—accelerates the decomposition of tin oxides, cassiterite, etc. The solution of the cassiterite will be complete in three or four minutes, but the heating is continued a little longer in order to burn off the carbon—C. A. Burghardt, *Chem. News*, **61**. 260, 1890; *Proc. Manchester Lit. Phil. Soc.* (4), **3**. 171, 1890; A. Gilbert, *Zeit. öffent. Chem.*, **16**. 441, 1910. This process also works well with chrome iron ore, wolframite, etc. H. T. Loram (*Proc. Chem. Soc.*, **27**. 60, 1910) recommends fusing the "tin ore" in a silver crucible, with six or seven times its weight of potassium hydroxide, and its own weight of potassium cyanide. Extract the cold mass with water. Dissolve all in dilute hydrochloric acid. Boil to expel cyanogen compounds, etc.

[5] Cassiterite may take 45 to 60 minutes—E. S. Simpson, *Chem. News*, **99**. 243, 1909; W. B. Giles, *ib.*, **99**. 1, 25, 1909; J. Gray, *Journ. Chem. Met. Soc. S. Africa*, **10**. 312, 1910; H. Milou and R. Fouret, *Int. Cong. App. Chem.*, 8. 373, 1912.

[6] Nickel crucibles are recommended for the determination of metals precipitated by hydrogen sulphide in acid solutions—tantalum, niobium, tin, etc.; silver crucibles for the determination of silica, alumina, iron, manganese, cerium, etc.

The heat required for the decomposition may be furnished by a reaction between the sodium peroxide and the organic matter of the substance[2] under investigation; or organic matter purposely added.[3] When starch and organic matter are used the fusion does not usually proceed quietly, but is attended by slight explosions which project the fused mass on to the sides and lid of the crucible. Walton and Scholz[4] observed that the fusion is much quieter if zinc sulphide be substituted for the starch, and Parr[5] found that the addition of a small amount of potassium persulphate led to better fusion and more complete decomposition. Suppose a lead frit be under investigation. The operation is conducted as follows:—

A round-bottomed nickel crucible about 30 c.c. capacity and 4 cm. in diameter is charged with 8 grms. of powdered sodium peroxide; 0·5 grm. of the finely powdered (200's lawn) frit; (say) 1·2 grm. of finely powdered zinc sulphide; and 0·3 grm. of potassium persulphate.[6] Each constituent must be quite dry,[7] and all thoroughly mixed by stirring with a glass rod. Partial mixing means partial decomposition. The rod is then brushed clean. The crucible is placed in a dish of cold water, taking care, of course, to keep the inside of the crucible dry. The cover is placed on the crucible a little to one side, so that a piece of lighted magnesium ribbon,[8] just over 1 cm. long, may be dropped into the crucible, and the cover placed in proper position immediately the mixture ignites. When the mass has cooled a little, about a minute after ignition, place the crucible in a clean evaporating basin, and add about 100 c.c. of cold water. When the violence of the reaction is over, the solution can be acidified with hydrochloric acid, and the silica determined by two evaporations in the usual manner.

For comparison purposes, two samples of a frit treated by the standard process gave 30·06 and 30·04 per cent. of silica; and two samples of the same frit, treated by the process just described, gave 29·98 and 30·06 per cent. of silica. The principal advantages of the method now under discussion are: (1) the vessel in which the decomposition occurs is much less attacked than usual—thus, an 18-gram crucible lost nearly 0·34 grm. in 16 fusions;[1] and (2) the whole process occupies but a few minutes. The mixing, ignition, cooling, and dissolution of the melted mass can be done in about 5 minutes.

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[1] J. Darroch and C. A. Meiklejohn, *Eng. Min. Journ.*, 82. 818, 1906; H. Angenot, *Zeit. angew. Chem.*, 17. 1274, 1904. For opening copper pyrites by fusion with six times its weight of potassium persulphate, see L. Majewski, *Kosmos*, 35. 597, 1910.

[2] S. W. Parr, *Journ. Amer. Chem. Soc.*, 22. 646, 1900; 30. 764, 1908 (coal in a steel bomb); H. H. Pringsheim, *Amer. Chem. Journ.*, 31. 386, 1903; *Ber.*, 37. 2155, 1904; 38. 2436, 1906 (halogens, arsenic, and phosphorus in organic compounds with a steel bomb).

[3] F. von Konek, *Zeit. angew. Chem.*, 17. 771, 1904; F. von Konek and A. Zöhls, *ib.*, 17. 1093, 1904; H. H. Pringsheim, *ib.*, 17. 1454, 1904.

[4] J. H. Walton and H. A. Scholz (*Amer. Chem. Journ.*, 29. 771, 1908; *Chem. News*, 98. 61, 76, 1908) used zinc sulphide either alone or mixed with iron pyrites—W. B. Pollard, *ib.*, 98. 211, 1908.

[5] S. W. Parr, *Journ. Amer. Chem. Soc.*, 24. 167, 1902.

[6] If lead be present, it will be found associated with the silica as lead sulphate.

[7] The mixture is so easily "ignited" that if any moisture be present, the heat evolved by the reaction with sodium peroxide suffices for the decomposition of the silicate.

[8] A piece of twine about 2 cm. long, soaked in alcohol, may be employed when the introduction of magnesia is not desired. There are many cases where the presence of zinc and sulphur is not particularly objectionable; in other cases such additions would present insuperable objections.

The method can be advantageously used for clays, galena,[2] lead glazes, lead slags, monazite sand, etc. The decomposition with basic substances like chromite, franklinite, and bauxite is not satisfactory. If the presence of iron be not objectionable, the chromite and franklinite can be completely decomposed by substituting 2·0 grms. of iron pyrites and 0·3 grms. of magnesium powder in place of the 1·2 grms. of powdered zinc sulphide. If the iron be objectionable, some other method of decomposition must be used. A similar remark applies to the addition of zinc sulphide.[3]

Reduction Process.—In the case of glazes containing tin oxide, it is sometimes advisable to subject the finely divided and dried material to a preliminary heating in a reducing atmosphere, as recommended by Wells,[4] in order to convert the oxide to metallic tin soluble in hydrochloric acid. The powdered material may or may not be first digested in hydrochloric acid and dried. A thin layer of the dried material is spread on the bottom of a porcelain boat—about 7 cm. long and 1 cm. broad. The boat is weighed, as usual, before and after the addition of the powder.[5] The boat is placed in a hard glass tube—about 30 cm. long and 2 cm. wide—drawn out at one end, as indicated at *A*, fig. 122. The wide end of the tube is connected by means of a perforated stopper with a wash-bottle and a Kipp's hydrogen apparatus; the opposite end of the tube is allowed to dip in a beaker containing dilute hydrochloric acid (1 : 10). The hydrogen is passed through a wash-bottle[6]—about two bubbles per second. When the air has been expelled from the tube, the gas jet[7] is lighted, and arranged so that about 15 cm. of the tube, in the neighbourhood of the boat, is heated to dull redness[8] for three or four hours. The boat is allowed to cool while the current of gas is still passing.[9] When cold, transfer the contents of the boat[10] to a 400-c.c. beaker, and treat the mass with 100 c.c. of hydrochloric acid with a few drops of nitric acid in order to convert the stannous into stannic chloride. Let the vessel stand in a warm place until the action has subsided. Boil 3 minutes. Dilute with an equal volume of hot water, and filter through a hot-water funnel (page 324). Ignite the filter paper and contents, and fuse[1] the residue with four or five times its weight of sodium carbonate and a gram of sodium nitrite in a platinum crucible. Take up the cold mass with hydrochloric acid and a drop of nitric acid. Mix the solution with that derived from the digestion of the "reduced" glaze with hydrochloric acid. Evaporate the solution to dryness for the separation of the silica (page 167). Nitric acid is sometimes preferred to hydrochloric acid to avoid dealing with the sparingly soluble lead chloride. If nitric acid be used with tin and antimony glazes, metastannic and antimonic acids will contaminate the silica.[2] If tin and lead be associated with the regular silica, alumina, magnesia, etc., precipitate the tin and lead as sulphides, as described below.

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[1] For the losses with direct fusions, see page 163.

[2] The galena is itself oxidisable (combustible), and the proportion of zinc sulphide may be accordingly reduced. Thus the charge for galena may be: 0·5 grm. powdered (200's lawn) ore; 8·0 grms. of sodium peroxide; 0·8 grm. zinc sulphide; 0·3 grm. potassium persulphate. Sulphuric acid was used for neutralising the alkaline solution, and sufficient acid to make about 2 per cent. excess H_2SO_4 was added. Sodium bisulphite was added to reduce the lead peroxide, and the solution boiled 5 minutes to get rid of the sulphur dioxide. The lead sulphate can then be determined gravimetrically, or volumetrically (molybdate process). The trial experiments were quite satisfactory.

[3] Unless some other sulphide be available.

[4] J. S. Wells, *School Mines Quart.*, **12.** 295, 1891; *Journ. Amer. Chem. Soc.*, **20.** 687, 1898; *Chem. News*, **64.** 294, 1891; M. W. Iles, *ib.*, **50.** 194, 1884; **85.** 179, 1902; A. Hilger and H. Haas, *ib.*, **63.** 195, 1891; *Ber.*, **23.** 458, 1890; J. A. Müller, *Bull. Soc. Chim.* (3), **25.** 1004, 1901; *Chem. News*, **85.** 147, 1902; W. Hampe, *Chem. Ztg.*, **11.** 19, 1887; H. W. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, **11.** 662, 1892; G. L. Mackenzie, *Trans. Inst. Min. Met.*, **13.** 87, 1903.

[5] The boat funnel of Stoltzenberg is convenient for filling boats with powder.

[6] That shown in the diagram is J. Habermann's (*Zeit. anal. Chem.*, **24.** 79, 1883).

[7] A Weston's cap on an ordinary Bunsen's burner is very convenient for this purpose, as shown in the diagram.

[8] The reduction of the tin oxide commences about 170°; lead oxide about 310°—W. Müller, *Pogg. Ann.*, **107.** 136, 1869. H. Haas (*Ueber die quantitative Trennung des Zinn's und Titan's*, Erlangen, 1890) separates tin from titanium by calcination of the mixture in a current of hydrogen, whereby tin alone is reduced to the metal and is subsequently dissolved by treatment with hydrochloric acid.

[9] Coal-gas may be used, but the objectionable sulphur, present in coal-gas, may form volatile sulphides with some of the constituents of the powder.

[10] The boat should not be heated high enough to vitrify the powder.

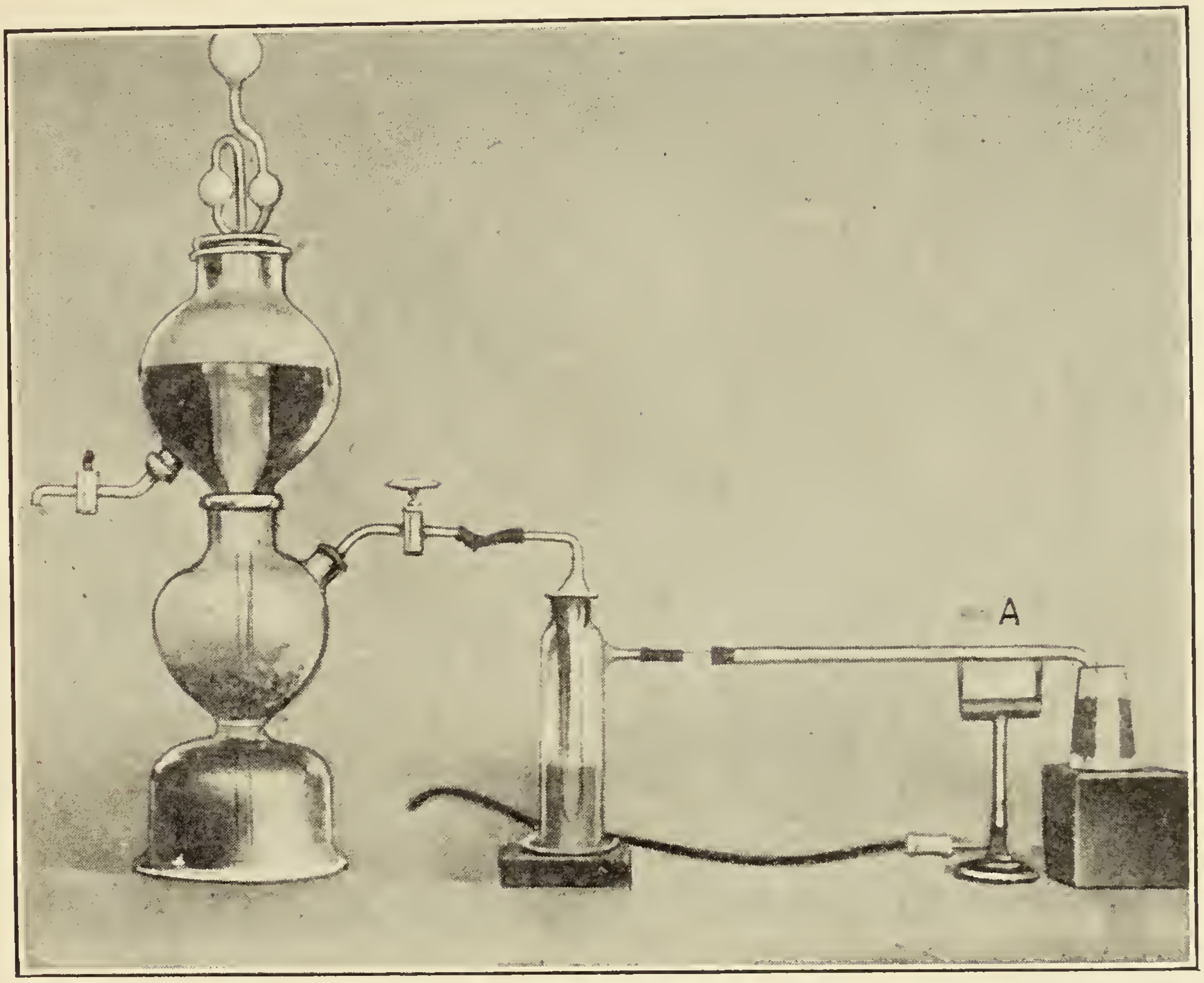

Fig. 122.—Opening lead and tin silicates by a preliminary reduction.

Fusion with Potassium Cyanide.—If tin and phosphorus be present, the silica may be contaminated with a metastannic phosphate (possibly $2SnO_2 . P_2O_5$).[3] In that case, the residue left after the ignition of the silica is treated with hydrofluoric acid to drive off the silica. After weighing, the residue is fused with at least three times its weight of pure potassium cyanide, free from sulphides, in a porcelain crucible. If the crucible be rotated and tapped while hot, the separate beads of tin will unite to form a larger bead. When cold, extract with water, filter, and wash the bead of metallic tin. The bead can be weighed as metal, or dissolved in hydrochloric acid, and added to the main solution. The difference between the weight of the tin calculated to SnO_2 and the weight of the "silica residue" may be taken as phosphoric oxide—P_2O_5. Or the filtrate from the tin can be boiled under a good hood with hydrochloric acid until the fumes of the highly poisonous cyanogen compounds have been driven off. Evaporate the solution to a small volume, and precipitate the phosphorus in the usual manner (page 595).[1]

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[1] It is not safe to assume that all the reducible oxides have been reduced to the metal and dissolved in the acids. A second treatment with the gas, or fusion of the residue as described in the text, is sometimes advisable.

[2] In that case, drive off the silica with hydrofluoric acid, and take up the residue by fusion with sodium carbonate, etc. Add the acid solution to the main solution.

[3] If arsenic be present, an insoluble metastannic arsenate soluble in hydrochloric acid may be formed.

The objection to this process turns on the fact that some tin may be lost owing to the formation of soluble alkali stannates. According to Bloxam,[2] if the potassium cyanide contains sulphide, an insoluble tin sulphide or a soluble thiostannate may be formed. If tungsten be present, it will be found in the solution as alkaline tungstate.

Fusion with Sodium Carbonate and Sulphur.—According to Miller,[3] the hydrogen reduction for the determination of tin in, say, cassiterite, gives low results, and he prefers Rose's process by fusion with sulphur and sodium carbonate. This Hofman conducts in the following manner:—Intimately mix 0·5 grm. of the sample with 3 grms. of a mixture of equal parts of sodium carbonate and sulphur[4] in a porcelain crucible (No. 1 Berlin), which, in turn, is placed in a larger porcelain crucible, and this again in a graphite crucible which has a layer of calcined fireclay spread on the bottom, so that the top of the crucible is nearly on a level with the top of the graphite crucible.[5] The whole is then heated in a crucible furnace for about 1–1½ hours at a red heat. The cold mass is treated with hot water. The tin dissolves as sodium thiostannate[6] along with some copper and iron. The latter will be precipitated by the addition of sodium sulphite to the deep-brown liquid.[7] Filter, wash with water containing sodium sulphite in solution, and finally with water containing hydrogen sulphide in solution. The precipitate contains iron, copper, and lead. The solution contains arsenic, antimony, and tin. These can be separated as described below. The objection to this process turns on the fact that it is tedious and dirty, particularly if a re-fusion be necessary.

Hydrofluoric Acid Process.—The problem with enamels and coloured glazes is often very difficult, since many metals of both the second and third groups may be present. If tin, bismuth, antimony, or arsenic be present, the hydrochloric acid evaporation for silica may cause an appreciable loss by volatilisation of the chlorides.[1] It may then be advisable to make a special decomposition for metals precipitated by hydrogen sulphide in an acid solution. This is often done with hydrofluoric acid.[2] Two grams of the impalpable powder are treated with about 20 c.c. of concentrated hydrofluoric acid (40 per cent.) and an equal volume of hydrochloric acid or nitric acid in a platinum dish, and the solution taken nearly to dryness.[3] If the residue[4] does not dissolve easily in hydrochloric acid, filter off the insoluble residue, and reduce the latter in coal-gas, as indicated above; or fuse it with sodium carbonate. Take up the cold cake with hydrochloric acid, and add the solution to the main filtrate. Separate the metals of the hydrogen sulphide group as indicated below.

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[1] H. Rose, *Pogg. Ann.*, **110**. 425, 1870; F. Oettel, *Chem. Ztg.*, **20**. 19, 1896; J. A. Müller, *Bull. Soc. Chim.* (3), **25**. 1004, 1901. The potassium cyanide fusion can also be employed for separating the metals reduced by this agent—W. H. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, **11**. 662, 1892; T. Moore, *Chem News*, **67**. 267, 1893; H. Y. Loram, *Proc. Chem. Soc.*, **27**. 60, 1912.

[2] C. L. Bloxam, *Journ. Chem. Soc.*, **18**. 97, 1865.

[3] E. H. Miller, *Journ. Anal. App. Chem.*, **6**. 441, 1892; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 286, 1851; H. O. Hofman, *Berg. Hütt. Ztg.*, **49**. 342, 350, 357, 1890; *Chem. News*, **62**. 57, 1890; *Tech. Quart.*, **3**. 112, 261, 1890; F. Becker, *Zeit. anal. Chem.*, **17**. 185, 1878; J. Mitchell, *Manual of Assaying*, London, 481, 1881; J. F. C. Abelspies, *Trans. Inst. Min. Met.*, **13**. 99, 1903; F. W. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, **11**. 662, 1892; E. D Campbell and E. C. Champion, *Ind. and Iron*, 267, 1898; O. Beck and H. Fischer, *School Mines Quart.*, **20**. 372, 1899; *Chem. News*, **80**. 259, 1899 (comparison of methods); L. Medri and C. Gastaldi, *Boll. chim. farm.*, **48**. 893, 1910.

[4] H. Rose's flux is a mixture of equal parts of sulphur and sodium carbonate. Chauvenet substituted potassium carbonate for the sodium carbonate. A. Froehde (*Pogg. Ann.*, **119**. 317, 1875) and E. Donath (*Zeit. anal. Chem.*, **19**. 23, 1880) prefer powdered sodium thiosulphate, which has previously been fused in order to remove the water.

[5] The object is to cut off the supply of air, otherwise decomposition will be incomplete.

[6] Gritty particles insoluble in water show that the action was not complete. In that case, filter, wash, dry, and repeat the treatment with the residue.

[7] Containing sodium polysulphide, which dissolves some iron and copper sulphides. Sodium sulphite changes sodium polysulphide to sodium monosulphide, in which iron and copper are practically insoluble.

§ 124. The Behaviour of Metals of the Hydrogen Sulphide Group in the Silica Determination.

Volatilisation of the Chlorides.

Care must be taken in boiling solutions—evaporation for silica, etc.—containing chlorides of arsenic, antimony, tin, bismuth, and mercury, since serious losses may occur by the volatilisation of the chlorides. Arsenious chloride, that is, arsenic trichloride, volatilises at 134°; antimony trichloride at 223°; and stannic chloride at 114°. But these compounds volatilise at a much lower temperature in steam which arises when the aqueous solutions are boiled.

(1) *Tin.*—Concentrated solutions of stannic chloride in the presence of hydrochloric acid (20 per cent.) lost, after 20 minutes' boiling at 107°, nearly 0·0014 grm. of $SnCl_4$. A solution of stannous chloride—$SnCl_2$—in hydrochloric acid can be evaporated to dryness without appreciable loss. Hence, the evaporation of stanniferous glazes, without arsenic and antimony, is best made in the presence of a reducing agent.

(2) *Antimony.*—A solution of antimony trichloride—$SbCl_3$—in hydrochloric acid (20 per cent.) may be heated to 110° without serious loss, but an appreciable quantity is volatilised at higher temperatures. Antimony trichloride is not so volatile under these conditions as stannic chloride. Antimony pentachloride, in hydrochloric acid (20 per cent.) solution, may be evaporated to dryness with a negligibly small loss. If, however, a mixture of stannous chloride and antimony pentachloride be added, the latter will be "reduced" and the former "oxidised" to the more volatile chlorides. According to Hoffmann, the addition of, say, 12 grms. of potassium chloride[5] retards from the volatilisation of these chlorides and permits these solutions to be evaporated without appreciable loss.

(3) *Arsenic.*—Arsenious chloride—$AsCl_3$—and arsenious salts in solutions containing hydrochloric acid are volatilised, during evaporation and boiling, in comparatively large quantities; but the arsenic salts can be evaporated to dryness with no appreciable loss. Hence the evaporation of antimonical and arsenical solutions is best made in the presence of an oxidising agent.[6]

(4) *Mercury.*—When 30 c.c. of aqueous 0·1 to 1·0 per cent. solutions of mercuric chloride are distilled, Minozzi[7] found that when half the liquid had

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[1] T. M. Drown and G. F. Eldridge, *Tech. Quart.*, 5. 136, 1893.

[2] H. N. Warren, *Chem. News*, 67. 16, 1983.

[3] Watch the hydrofluoric acid for "lead" impurity.

[4] A bluish residue indicates tungsten.

[5] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 10, 1911.

[6] J. I. D. Hinds, *Inter. Cong. App. Chem.*, 8. 227, 1912.

[7] A. Minozzi, *Boll. Chim. Farm.*, 43. 745, 1904; E. Esteve, *Chem. Ztg.*, 35. 1152, 1911; P. Bohrisch and F. Kürschner, *Pharm. Centralhalle*, 52. 1367, 1911.

distilled over, the distillates contained from 0·00025 to 0·0022 grm. of mercuric chloride. The greater the concentration of the solution, the greater the loss by volatilisation. The error introduced into an analysis, under these conditions, may amount to 0·2 per cent. Similar results were obtained in the presence of hydrochloric and phosphoric acids, and sodium chloride.

Separation of Insoluble Constituents with the Silica.

The silica residue may be very complex. Insoluble tin phosphates, tin arsenates, antimony and bismuth compounds,[1] etc., may separate with the silica. The determination of the silica is therefore liable to error. In view of these difficulties, it is better to determine the members of the hydrogen sulphide group on a separate sample by, say, the hydrofluoric acid process of decomposition, page 270. With the portion in which the members of the hydrogen sulphide group are not being determined, losses during the evaporation for silica and after the silica has separated may be neglected. In the analysis of stanniferous slags, containing tin, in addition to the usual constituents of clays, Bailey[2] evaporates the solution from the sodium carbonate fusion to dryness with 20 c.c. of concentrated nitric acid; and boils the residue with 20 c.c. of concentrated hydrochloric acid.[3] The insoluble residue of stannic oxide and silica is mixed with an equal volume of water; two sticks of zinc—about $2\frac{1}{2}$ cm. long—are placed in the mixture, and the whole is allowed to stand in a warm place for some time. Carefully scrape off any adherent spongy tin from the sticks of zinc; filter and wash the tin and silica, and transfer the insoluble mixture back from the filter paper into the dish. Add 10 c.c. of concentrated hydrochloric acid and a few drops of nitric acid,[4] and warm the mixture until the silica appears white. Dilute the solution, filter, and wash. The silica and tungsten oxide will be found on the filter paper;[5] the tin, etc., in the filtrate.

Dott[6] separates stannic oxide from the silica by heating the mixture with three or four times its weight of hypophosphorous acid over a Bunsen's flame for about 30 minutes. The tin is converted into a stannous phosphate soluble in warm hydrochloric acid. The silica is not affected by this treatment, and can be filtered off.

§ 125. The Theory of Precipitation by Hydrogen Sulphide.

The terms "soluble" and "insoluble" are purely relative. With increasing refinements in the methods of measurement, the list of substances insoluble in a given solvent becomes shorter and shorter. Many substances once said to be "insoluble" in a given solvent are known to be appreciably soluble. It is all a question of delicacy of measurement. Hence, some leap beyond the domain of demonstrated fact, and say, "No substance is perfectly insoluble in water."

The method of classifying certain elements into two groups—those which form soluble and those which form insoluble sulphides in hydrochloric acid—frequently conveys wrong ideas of the properties of the sulphides. The solubility of the sulphides depends upon the concentration of the acid. For instance, if hydrogen sulphide be passed into 5 c.c. of a solution of 2 grms. of tartar emetic in 15 c.c. of hydrochloric acid (sp. gr. 1·175) and 85 c.c. of water,[1] antimony sulphide will be precipitated, but not if 12 c.c. of hydrochloric acid with no further addition of water had been employed. In the one case, the reaction may be represented $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$; and, in the second case, $Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3$. In other words, the antimony sulphide, in the second case, is decomposed as fast as it is formed. Similarly, no lead will be precipitated by hydrogen sulphide from a solution containing over 3 per cent. of hydrochloric acid (HCl), and if the solution has 2·5 per cent. of acid, the lead will be imperfectly precipitated: part will be precipitated, and a certain proportion will be decomposed as fast as it is formed, and thus remain in solution. Similarly a 5 per cent. boiling solution of hydrochloric acid will prevent the precipitation of cadmium.[2]

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[1] Also tungsten, niobium, and tantalum compounds, if these elements be present.

[2] H. Bailey, *Chem. News*, 73. 88, 1896.

[3] There is no danger of losing tin, because it is here insoluble.

[4] Just sufficient to oxidise the tungsten, if any be present.

[5] Separate by the ammonia process, page 409.

[6] D. B. Dott, *Pharm. Journ.*, 81. 585, 1908.

If, then, a metallic sulphide be treated with hydrochloric acid, hydrogen sulphide and a metallic chloride will be formed:

$$RS + 2HCl \rightleftharpoons RCl_2 + H_2S.$$

Conversely, when a metallic chloride in aqueous solution is treated with hydrogen sulphide, the metallic sulphide and hydrochloric acid are produced:

$$RCl_2 + H_2S \rightleftharpoons RS + 2HCl.$$

Hydrochloric acid thus accumulates in the solution as the action goes on. After the hydrochloric acid has attained a certain concentration, if any more sulphide is produced, the excess of sulphide will be decomposed by the acid. There are thus two simultaneous reactions: (1) formation of sulphide and hydrochloric acid; and (2) formation of chloride and hydrogen sulphide. In further illustration, if a current of hydrogen sulphide be passed through a saturated solution of zinc chloride, part of the metal is precipitated; but when the hydrochloric acid has attained a certain concentration, the action apparently ceases because the reverse change sets in. Hence, the precipitation of the zinc as sulphide will be incomplete.[3] Similar remarks apply for the other metals.

We can get more precise ideas than this. Take the case of lead chloride:

$$PbCl_2 + H_2S \rightleftharpoons PbS + 2HCl.$$

When equilibrium is established,[4] the solution contains lead chloride, hydrogen sulphide, and hydrochloric acid. If bracketed chemical symbols be employed to represent the concentration (gram-molecules per litre) of the respective compounds *in solution*, the law of mass action[1] requires that the product of the concentration of the given chloride and concentration of the hydrogen sulphide, divided by the square of the concentration of the hydrogen chloride, shall always have the same value.[2] In symbols, for equilibrium, we have

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[1] The solution of tartar emetic will keep a couple of hours.

[2] M. Martin, *Journ. prakt. Chem.* (1), **67**. 374, 1856; C. C. Hutchinson, *Phil. Mag.* (5), **8**. 433, 1879; *Chem. News*, **41**. 28, 1880. In separating cadmium from zinc by hydrogen sulphide in an acid solution, some prefer to precipitate most of the zinc with the cadmium, and then digest the precipitate in a solution containing about 5·5 per cent. of hydrochloric acid without heating, but with vigorous agitation. It is claimed that the zinc passes into solution, and the excess of hydrogen sulphide in the solution prevents the dissolution of the cadmium.

[3] M. Baubigny, *Compt. Rend.*, **107**. 1148, 1888; G. Chesneau, *ib.*, **111**. 269, 1890. In the case of zinc, the accumulation of hydrochloric acid can be prevented by the use of certain organic salts—ammonium or sodium acetate, sodium formate, etc. These substances react with the hydrochloric acid, producing sodium chloride and an acetate (or formate, etc.). This is a very convenient way of substituting a weak acid—say, acetic acid or formic acid—for a strong acid—hydrochloric acid. The solubility of the zinc sulphide in, say, acetic acid is so small that inappreciable amounts of zinc remain in solution, although iron, nickel, cobalt, and manganese sulphides are dissolved by the acid.

[4] At an early stage in the reaction between hydrogen sulphide and lead chloride, lead thiochloride—probably $PbS . PbCl_2$—appears to be formed, since a brick-red precipitate of this compound sometimes separates when hydrogen sulphide is passed into a solution of lead chloride in hydrochloric acid.—E. H. E. Reinsch, *Journ. prakt. Chem.* (2), **13**. 130, 1876; V. Lehner, *Journ. Amer. Chem. Soc.*, **23**. 680, 1901; F. Parmentier, *Compt. Rend.*, **114**. 298, 1892.

$$\frac{[\mathrm{PbCl_2}]\times[\mathrm{H_2S}]}{[\mathrm{HCl}]^2} = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This agrees with facts, and when the phenomenon is described in this way, it is easy to see that if the concentration of the acid be increased, and the concentration of the hydrogen sulphide be constant, the amount of lead chloride which remains in a given solution (*i.e.* escapes precipitation) must increase in order to keep the numerical value of the ratio constant. Conversely, if it be desired to keep the amount of lead chloride in the solution as low as possible, it is necessary to keep the concentration of the acid down to a minimum value.[3] The concentration of the hydrogen sulphide in solution is practically constant (0·0073 gram-molecule per litre at 20°) when the gas is passing through the solution. If the concentration of the hydrogen sulphide in solution were large, and the concentration of the metallic chloride in solution small, a very small excess of acid would not suffice to keep the metals in solution. It will be observed, however, that the concentration of the hydrogen sulphide under ordinary conditions is small. In consequence, a comparatively small amount of acid is sufficient to prevent the separation of sulphides of zinc, iron, and manganese. This may be expressed another way: if the solubility of the hydrogen sulphide had been greater than it is, some of the metals—zinc, iron, nickel, etc.—would have been included in the "hydrogen sulphide" group; and, conversely, had the solubility of the hydrogen sulphide been less than it is, some of the present members of the "hydrogen sulphide" group would not have been there—for instance, stannous tin, lead, cadmium. These deductions have been experimentally realised by Bruni and Padoa.[4] By causing the hydrogen sulphide to react under pressure, the solubility of the hydrogen sulphide in the liquid was augmented, and iron, nickel, and cobalt were precipitated; by working under diminished pressure, the solubility of the hydrogen sulphide in the acid liquid was reduced, and cadmium was not precipitated under conditions where otherwise the sulphide would have separated.

Under ordinary conditions, the solubility[5] of the precipitated sulphides in dilute hydrochloric acid, starting with the least soluble,[6] is approximately as follows—reading from above downwards:—

Molybdenum
Platinum
Gold
Arsenic
Silver
Copper
Antimony

Bismuth
Stannic tin
Mercury
Cadmium
Lead
Stannous tin

Zinc
Titanium
Iron
Nickel
Cobalt
Manganese

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[1] J. W. Mellor, *Chemical Statics and Dynamics*, London, 156, 1904.

[2] Neglecting disturbances due to the presence of foreign substances in the solution.

[3] This, of course, is limited by the necessity for keeping the zinc in solution, when separating lead and zinc by this method.

[4] G. Bruni and M. Padoa, *Atti Accad. Lincei* (5), **14**. ii. 525, 1905.

[5] The term "solubility" is here understood to refer to the amount of the element which remains in solution, or escapes precipitation, when the hydrogen sulphide is passed through an acid solution of a given concentration. The order of solubility will be the same as if the numerical values of the constants of the series indicated in equation (1) above were arranged in ascending order.

[6] The order is only approximate, and varies with the strength of the acid. For the solubility of the sulphides in water, see O. Weigel, *Zeit. phys. Chem.*, **58**. 293, 1907; W. Böttger, *ib.*,

Elements wide apart in the list can be easily separated by hydrogen sulphide in acid solution, but elements close together require a very careful adjustment of the amount of acid in solution before satisfactory separations can be made. For instance, the separation of cadmium or lead from zinc by means of hydrogen sulphide is only satisfactory when the concentration of the acid is very carefully adjusted. If too much acid be present, cadmium or lead will be imperfectly precipitated; while if too little acid be present, zinc will be precipitated with the cadmium or lead.[1] Hence, no sharp line of demarcation can be drawn between metals precipitated and metals not precipitated by hydrogen sulphide in acid solution. All depends upon the concentration of the acid.[2] This is conveniently adjusted so that the lead and stannous sulphides are precipitated, while zinc sulphide remains in solution. A solution containing 4 c.c. of hydrochloric acid (sp. gr. 1·12) per 100 c.c. will serve this purpose.[3] If more acid be present, there will be a danger of incomplete precipitation of stannous tin and lead; if less than this amount of acid be present, some zinc, iron, nickel, cobalt, or manganese may be precipitated. The adjustment of the acid cannot be perfect, but it can generally be made so that inappreciable quantities of the sulphides to be precipitated remain in solution. This is illustrated by fig. 123, which shows the relation between the amount of antimony chloride which remains in solution in the presence of hydrochloric acid and the concentration of this acid when the solution is saturated with hydrogen sulphide. The proximity of the curve to the lower horizontal axis shows that for 20 grms. and less hydrochloric acid per 100 grms. of solution, very little antimony will escape precipitation.

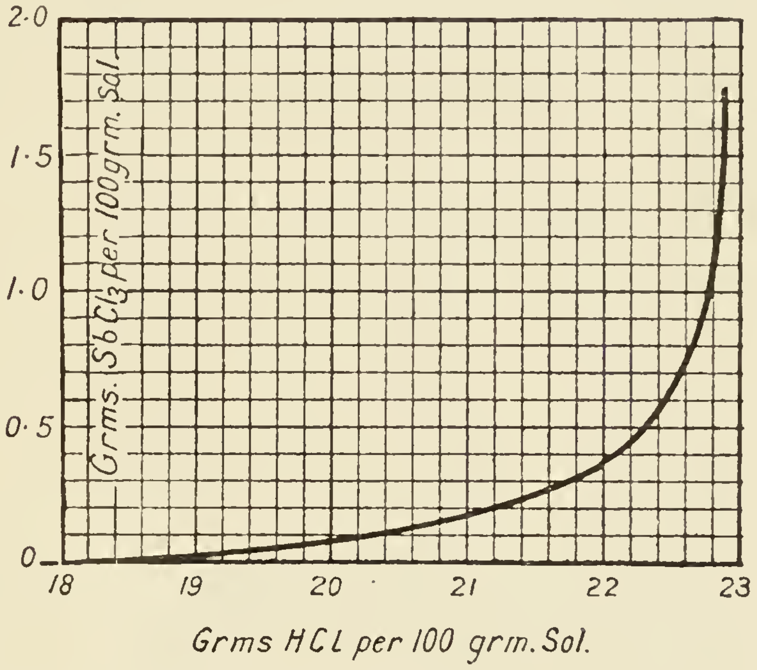

FIG. 123.—Effect of hydrochloric acid on the solubility of antimony sulphide.

Filtration.—In washing sulphide precipitates, say, copper sulphide in acid solution, with hydrogen sulphide water, a colourless filtrate is usually obtained. As the concentration of the acid in the mother liquid diminishes by washing, the filtrate sometimes becomes turbid, and, in the case of copper, the filtrate may be tinted green.[4] There are several distinct actions going on. First, the

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46. 531, 1903; M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 49, 1911.

[1] A. W. Hofmann (*Liebig's Ann.*, **115.** 286, 1860; *Journ. Chem. Soc.* **13.** 78, 1860) separates copper and cadmium sulphides with sulphuric acid (1 : 5)—the latter alone dissolves.

[2] L. Loviton (*Journ. Pharm. Chem.* (5), **17.** 361, 1888; *Zeit. anal. Chem.*, **29.** 345, 1890) has devised a method for separating antimony and tin based upon the solubility of the sulphides in hydrochloric acid of different concentrations; and E. Neher's process (*Zeit. anal. Chem.*, **32.** 45, 1893) for the separation of arsenic, antimony, and tin is based on the same property. A. A. Abel and F. Field, *Journ. Chem. Soc.*, **14.** 290, 1862; F. Field, *Chem. News*, **3.** 114, 1861; A. H. Low, *Journ. Amer. Chem. Soc.*, **28.** 1715, 1906; O. Köhler, *Arch. Pharm.* (3), **27.** 406, 1889; G. Panajotow, *Ber.*, **42.** 1296, 1909; E. Lesser, *Ueber einige Trennungs und Bestimmungs-Methoden des Arsens, des Antimons, und des Zinns*, Berlin, 1886; W. R. Lang and C. M. Carson, *Journ. Soc. Chem. Ind.*, **21.** 1018, 1902; with J. C. Mackintosh, *ib.*, **21.** 748, 1902; J. and H. S. Pattinson, *ib.*, **11.** 211, 1898; F. Kietreiber, *Osterr. Chem. Ztg.* (2), **13.** 146, 1910.

[3] A. A. Noyes and W. C. Bray, *Journ. Amer. Chem. Soc.*, **29.** 137, 1907; *Tech. Quart.*, **19.** 191, 1906.

[4] The filtrate becomes darker in colour, and finally flakes of copper sulphide separate from the filtrate.

sulphide is oxidised to sulphate[1]; second, the colloidal sulphides may be deflocculated (page 96); and, third, if water alone be used in the washing, the dilution of the mother liquid may lead to the precipitation of some of the elements belonging to the next group, say, zinc sulphide, and so contaminate the precipitate being washed. Hence, the washing liquid should be kept acidified.[2]

§ 126. The Separation of the Metals precipitated by Hydrogen Sulphide in Acid Solutions.

In the extreme case, suppose that a qualitative examination shows that the filtrate from the silica contains antimony, arsenic,[3] lead, bismuth, cadmium, tin, and copper, as well as alumina, etc. Adjust the solution so that it contains 10 c.c. of hydrochloric acid (sp. gr. 1·12) per 100 c.c. Heat the solution in an Erlenmeyer's flask at 70° to 80°, and pass hydrogen sulphide through the hot solution[4] for about an hour while the temperature of the solution is maintained.[5] Let the mixture cool. When cold, add one and a half times its own bulk of water (100 c.c. becomes 250 c.c.),[6] and saturate in the cold with hydrogen sulphide passing in a slow stream for about 15 minutes. Cork the flask and let the solution stand two or three hours. Filter and wash the precipitate with a dilute acid solution containing 20 c.c. hydrochloric acid (sp. gr. 1·12) per litre and saturated with hydrogen sulphide.

The precipitate may contain lead, bismuth, copper, cadmium, arsenic, antimony, and tin sulphides. The precipitate will generally be practically free from aluminium, iron, zinc, nickel, cobalt, and manganese. The filtrate is used for the determination of the alumina, etc. (page 177).[1]

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[1] Hence, the filtration should be conducted as rapidly as possible, and the filter paper with the precipitate should be kept filled with the hydrogen sulphide wash-water.

[2] G. Larsen, *Zeit. anal. Chem.*, **17**. 312, 1878; E. Berglund, *ib.*, **22**. 184, 1883; W. Dederichs, *Pharm. Ztg.*, **44**. 178, 1899. Mineral acids are objectionable if the filter paper is to be afterwards dried, because the acid is concentrated on the paper during the drying, and the paper is attacked. The paper then readily disintegrates. A dilute solution of acetic acid, saturated with hydrogen sulphide, gives good results.

[3] According to F. Wöhler, more or less zinc sulphide is precipitated in the presence of arsenic acid in comparatively strongly acid solutions, but not if arsenious acid be present. For this reason, and the reason stated in the next footnote, it is well to reduce the arsenic to arsenious salts, if arsenic salts be present.

[4] Elements at the upper end of the series, page 274, are precipitated more or less imperfectly in the cold. Arsenic sulphide, for instance, continues separating a long time after the solution is saturated, hence the current of gas is continued an hour longer. The sulphides which separate from a hot solution can be filtered and washed more easily than precipitates formed in cold solutions. Arsenious acid—H_3AsO_3—reacts at once with hydrogen sulphide, forming As_2S_3; with arsenic acid—H_2AsO_4—the formation of As_2S_3 is the joint effect of three consecutive reactions: (1) the formation of thioarsenic acid—H_3AsSO_3; this (2) slowly decomposes into sulphur and arsenious acid—H_3AsO_3; this latter (3) reacts with the hydrogen sulphide, as indicated above. Hence, the initial and end products are represented by the equation: $2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O$. One object of the boiling is to accelerate the very slow decomposition of the thioarsenic acid. Hence, before passing the hydrogen sulphide, some prefer to reduce the arsenic acid to arsenious acid with sulphur dioxide, or by warming the solution with a mixture of hydrochloric acid and hydriodic acid (or potassium or ammonium iodide)—sulphur dioxide is not recommended as a reducing agent—L. L. de Koninck, *Bull. Soc. Chim. Belg.*, **23**. 88, 1909. There is also a very slow side reaction—$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$—particularly in cold, feebly acid solutions (J. P. Bouquet and S. Cloiz, *Ann. Chim. Phys.* (3), **13**. 44, 1845; B. Brauner and F. Tomiczek, *Monats. Chem.*, **8**. 607, 1887; L. R. W. McCay, *Journ. Amer. Chem. Soc.*, **24**. 661, 1902; *Zeit. anal. Chem.*, **27**. 632, 1888; F. Neher, *ib.*, **32**. 45, 1893; R. Bunsen, *Liebig's Ann.*, **192**. 305, 1878; H. Rose, *Pogg. Ann.*, **107**. 186, 1859).

[5] The current of gas passes at the rate of about two bubbles per second.

[6] If sulphuric acid be used in place of hydrochloric acid, use 3·75 c.c. of sulphuric acid (sp. gr. 1·84) with the same dilutions. The greater acidity of the boiling solution prevents the separation of titanium hydroxide during the boiling. The acid is also useful in preventing the separation of bismuth and antimony oxychlorides. The great dilution required for the separation of lead and stannous tin would lead to the precipitation of the oxychlorides in question.

Precipitation in Pressure Flasks.—When molybdenum, platinum, gold, or selenium are present, the solution to be treated with hydrogen sulphide is placed in a thick-walled mineral water bottle (or "pressure flask"),[2] heated nearly to boiling, and saturated with hydrogen sulphide. The solution is cooled and saturated, in the cold, with hydrogen sulphide. Close the bottle with a cork and wire, or screw the stopper down as at *D*, fig. 124. Heat the bottle in a vessel of water for about an hour. The pressure bottle should not rest directly on the bottom of the water bath, but rather be suspended by a wire *C*, fig. 124, so that it is immersed up to the neck in the cold water. The water bath is gradually heated until the water boils. Boiling water is added to the bath, if necessary, as the water evaporates. The new water should not be poured directly on to the pressure bottle. At the end of the experiment, the water bath is allowed to cool; the bottle is then removed from the bath, and opened. Fig. 124 shows a Linter's "pressure flask" *A* ready for lowering into the bath *B*. The bottle can be surrounded with a stout wire gauze so that no damage may be done if it bursts. Molybdenum, platinum, gold, selenium (also tellurium), if present, will be found with the precipitated sulphides of tin, arsenic, antimony, lead, cadmium, etc.

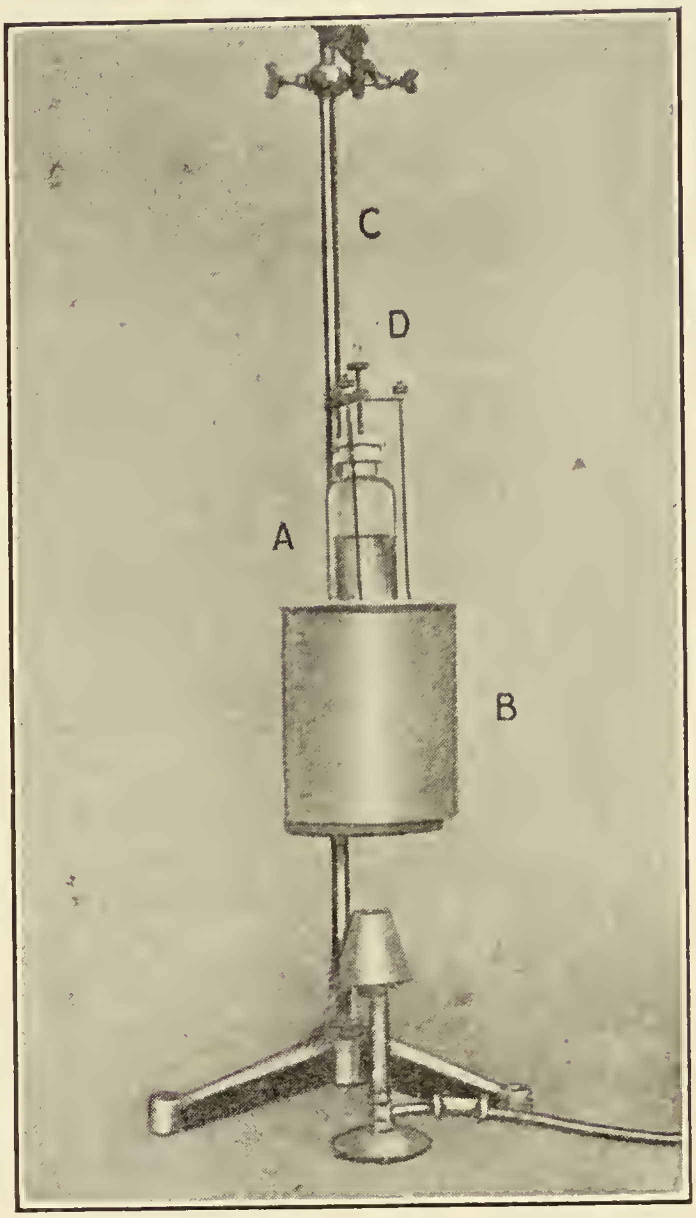

FIG. 124.—Linter's "pressure flask."

§ 127. The Separation of Tin, Arsenic, and Antimony from the remaining Metals.

The precipitate is now treated with a concentrated aqueous solution of sodium monosulphide[3] in a covered beaker heated to about 70°. The lead, copper,[1] cadmium,[2] and bismuth[3] present remain undissolved, while the arsenic, antimony, and tin pass into solution.[4] The precipitate is washed with the sodium sulphide solution. The arsenic, antimony, and tin in the solution are separated by the methods indicated below; the precipitate is dissolved in hydrochloric acid, and the lead, bismuth, copper, and cadmium are also separated one by one, as indicated later on. If one or more of the elements in question be absent, the corresponding steps are omitted. Short cuts are also advisable in special cases.

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[1] The hydrogen sulphide must be boiled off from the filtrate, and the free sulphur removed by filtration. The iron is oxidised with a few drops of nitric acid, or hydrogen peroxide, or bromine water.

[2] Pressure flasks—Linter's, Salamon's, etc.—are made specially for the purpose. A. Gawalovski, *Zeit. anal. Chem.*, **22**. 526, 1883; F. Allihn, *ib.*, **23**. 406, 1884; H. Rempel, *Ber.*, **18**. 621, 1885; A. Eiloart, *Chem. News*, **55**. 148, 1887. See also page 412.

[3] SODIUM MONOSULPHIDE SOLUTION.—This reagent is prepared as follows:—Dissolve 333 grms. of pure sodium hydroxide (made from the metal) in a litre of air-free water. Pour the solution into a flask, and pass a rapid stream of washed hydrogen sulphide into the solution through a wide glass tube (1 cm. bore) fitted into a double-bored stopper, so as to protect the contents of the flask from air as much as possible. The object of the wide delivery tube is to avoid choking the tube with the separated sulphide. There is an increase in the volume of the solution such that 1000 c.c. becomes 1218 c.c. When the solution is saturated, the pale yellow liquid may be poured into small glass-stoppered bottles and sealed with paraffin; or the solution may be evaporated in a platinum or porcelain dish until a film of crystals begins to

It must also be added that in many technical analyses, *it is not usual to work through a complex series of separations with one portion of a given sample, but several separate portions are taken and one group of constituents in each portion is determined by special methods of isolation.* In a long series of separations, some of the stages may be more suited for one element than for another, and a process of analysis is selected which gives the best average for all the constituents to be determined, and not the one most suited for any particular constituent. When, however, a separate portion of the original sample is taken for the determination of each constituent, a method of separation specially favourable for that constituent can be employed.

Theoretical.—Freshly precipitated arsenic, antimonic, and stannic sulphides are quickly dissolved by sodium sulphide;[5] stannous sulphide is but slowly dissolved.[6] Soluble alkaline thioarsenate—$AsS(SNa)_3$; thioantimoniate—$SbS(SNa)_3$; and thiostannate—$SnS(SNa)_3$—appear to be formed; while arsenious and antimonious sulphides form the corresponding $As(SNa)_3$ and $Sb(SNa)_3$ respectively.[7]

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form on the surface, and the hot liquid bottled and sealed. The liquids may deposit crystals of sodium monosulphide—$Na_2S . 9H_2O$—on standing or cooling. The bottled solutions keep indefinitely when protected from the atmospheric air. A small quantity of black iron, nickel or silver sulphide, may settle on the bottoms of the bottles on standing. For use, the solution is diluted to a specific gravity 1·14. Sodium hydroxide pure by alcohol does not give so satisfactory a solution as that prepared from the metal, since a solution prepared from the former will be coloured with colloidal sulphides, which only separate after long standing. According to E. Prothière and A. Revaud (*Journ. Pharm. Chim.*, **16**. 484, 1902), a layer of almond or olive oil on the surface of a solution of the sulphide cuts off the air without forming deposits or an emulsion. The solution then keeps indefinitely. For the action of polysulphides see H. Schiff, *Liebig's Ann.*, **115**. 68, 1860.

[1] Freshly precipitated copper sulphide is appreciably soluble in colourless ammonium sulphide, and still more soluble in yellow ammonium sulphide—C. L. Bloxam, *Journ. Chem. Soc.*, **18**. 94, 1865.

[2] A. Ditte (*Compt. Rend.*, **85**. 402, 1887; *Chem. News*, **36**. 109, 1877) says that cadmium sulphide is appreciably soluble in ammonium sulphide, but E. Donath and J. Mayerhofer (*Zeit. anal. Chem.*, **20**. 384, 1881) state that this is not the case. H. Fresenius (*Zeit. anal. Chem.*, **20**. 26, 1681) agrees with Ditte. G. Vortmann, *Monats. Chem.*, **1**. 952, 1880; E. Zettnow, *Pogg. Ann.*, **130**. 328, 1867.

[3] T. B. Stillmann (*Journ. Amer. Chem. Soc.*, **18**. 683, 1896) showed that if a solution containing bismuth be made alkaline with sodium hydroxide, and then heated with an excess of sodium sulphide, a considerable amount of bismuth remains in solution; but G. C. Stone (*ib.*, **18**. 1091, 1896) pointed out that if the bismuth sulphide be first precipitated from an acid solution, it is not dissolved by subsequent treatment with an alkaline sulphide. J. Knox, *Journ. Chem. Soc.*, **95**. 1760, 1909.

[4] Molybdenum, gold, platinum, and selenium, if present, may be partly dissolved with the arsenic, etc., and partly retained by the insoluble sulphides.

[5] R. Bunsen, *Liebig's Ann.*, **192**. 320, 1878; H. Thiele, *ib.*, **265**. 65, 1891; B. Brauner and F. Tomiczek, *Monats. Chem.*, **8**. 607, 1887; F. Neher, *Zeit. anal. Chem.*, **32**. 45, 1893; L. R. W. M'Cay, *ib.*, **27**. 632, 1888; **34**. 725, 1895; R. Fresenius, *ib.*, **1**. 192, 1862; J. J. Berzelius, *Pogg. Ann.*, **7**. 1, 1826; C. Rammelsberg, *ib.*, **52**. 191, 1841; C. F. Nilson, *Journ. prakt. Chem.* (2), **14**. 149, 1877; (2), **19**. 170, 1879.

[6] Hence, some use a little nitric acid with the hydrochloric acid in order to oxidise the stannous sulphide and accelerate the rate of solution.

[7] Gold and platinum sulphides, in the same group as arsenic sulphide, dissolve with difficulty in the alkaline sulphide, and thus form an intermediate link between sulphides soluble and

Sodium monosulphide, in aqueous solution, is partly hydrolysed or decomposed by water, forming sodium hydroxide and hydrosulphide:

$$Na_2S + H_2O \rightleftharpoons NaOH + NaHS.$$

The amount of hydrolysis depends upon the concentration of the solution. With dilute solutions, say $\frac{1}{10}$N-solution, 86·4 per cent of the Na_2S is hydrolysed,[1] but with increasing concentrations the amount of hydrolysis is diminished. Solutions of sulphur in the alkaline sulphides are much less hydrolysed than the monosulphide. This question of hydrolysis is important, because the products of hydrolysis may attack sulphides[2] which would otherwise be insoluble. Aqueous solutions of ammonium monosulphide are more readily hydrolysed than sodium monosulphide; and, in consequence, sodium monosulphide is preferable to the ammonium salt, particularly in the presence of copper sulphide, which is slightly soluble in ammonium monosulphide. On the other hand, the ammonium salt is nearly always used if mercury salts be present, because mercuric sulphide is insoluble in ammonium monosulphide,[3] but readily soluble in sodium or potassium monosulphides owing to the formation of a thio-salt:

$$HgS + Na_2S = Hg(SNa)_2.$$

The mercuric sulphide is soluble in ammonium sulphide if a little potassium or sodium hydroxide be present;[4] and it is also more readily soluble in potassium or sodium sulphide if a little of the alkaline hydroxide be also present.[5] The latter reaction enables mercury sulphide to be separated from the sulphides of lead, silver, bismuth, and copper.

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sulphides insoluble in the alkaline sulphide. According to J. Riban (*Compt. Rend.*, 85. 283, 1877; *Bull. Soc. Chim.* (2), 28. 241, 1877), platinum sulphide—PtS_2—alone is practically insoluble in ammonium and sodium mono- and polysulphides. In the presence of arsenic, antimony, and tin sulphides, appreciable quantities of platinum and gold sulphides pass into solution, and this the more the greater the quantity of those elements present. The separation of gold and platinum, as well as molybdenum and selenium, is not therefore satisfactory by this process, since part will be found in the solution, and part with the precipitate.

[1] F. W. Küster and E. Heberlein, *Zeit. anorg. Chem.*, 43. 53, 1905; J. Walker, *Zeit. phys. Chem.*, 32. 137, 1900; H. Rose, *Pogg. Ann.*, 55. 533, 1842; C. F. Sammet, *An Investigation on the Production, Precipitation, and Migration of Colloids*, Boston, Mass., 1903.

[2] This, for instance, is the case with copper sulphide in ammonium monosulphide, and particularly with ammonium polysulphide. Copper and lead are also attacked by sodium polysulphides, apparently not altogether because of the hydrolysis. The mode of action of the polysulphides has not yet been made quite clear. According to V. Hassreidter (*Zeit. angew. Chem.*, 18. 292, 1905), the copper can be recovered from a solution of the sulphide in, say, sodium polysulphide by boiling the solution with the cautious addition of sodium sulphite until colourless; sodium monosulphide and thiosulphate are formed, which have no solvent action on copper sulphide.

[3] But slightly soluble in ammonium polysulphide—A. Claus, *Liebig's Ann.*, 129. 209, 1863; *Chem. News*, 9. 145, 1864; C. Barfoed, *Journ. prakt. Chem.* (1), 93. 230, 1865; *Zeit. anal. Chem.*, 3. 139, 1864; 4. 435, 1865.

[4] J. Volhard, *Liebig's Ann.*, 255. 252, 1891.

[5] A. Ditte, *Compt. Rend.*, 98. 1271, 1884; K. Polstorff and C. Bülow, *Arch. Pharm.*, 229. 292, 1891.

CHAPTER XXI.

THE DETERMINATION OF ARSENIC.

§ 128. The Separation of Arsenic from Antimony and Tin by Distillation.

THE distillation process, proposed by Schneider and by Fyfe, depends upon the volatility of arsenious chloride.[1] If arsenic compounds be reduced to arsenious compounds in hydrochloric solution by ferrous sulphate, Fischer[2] showed that the arsenic may be quantitatively separated as arsenious chloride from solutions containing antimony and tin.[3] By this means arsenic may also be separated from the other metals of the hydrogen sulphide group.[4] Details of the modified Fischer's process are as follows:—

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[1] See page 271.

[2] E. Fischer, *Ber.*, **13.** 1778, 1880; *Liebig's Ann.*, **208.** 182, 1881; A. Classen and R. Ludwig, *Ber.*, **18.** 110, 1885; F. Hufschmidt, *ib*, **17.** 2245, 1884; *Chem. News*, **50.** 269, 1884; W. Odling, *ib.*, **8.** 27, 1863; T. Gibb, *ib.*, **45.** 218, 1882; F. C. Schneider, *Pogg. Ann.*, **85.** 433, 1852; A. Fyfe, *Phil. Mag.* (4), **2.** 487, 1851; *Journ. prakt. Chem.* (1), **55.** 103, 1852; P. Jannasch and E. Heimann, *ib.* (2), **74.** 473, 488, 1906; O. Ducru, *Compt. Rend.*, **127.** 227, 1898; *Chem. News*, **78.** 73, 1898; A. Hollard and L. Bertiaux, *ib.*, **81.** 242, 1900; *Bull. Soc. Chim.* (3), **23.** 300, 1900; A. Hollard, *ib.* (3), **23.** 292, 1900; *Chem. News*, **81.** 258, 1900; E. Azzarello, *Gazz. Chim. Ital.*, **39.** ii, 450, 1910; J. Clark, *Journ. Soc. Chem. Ind.*, **6.** 353, 1887; A. Gibb, *ib.*, **20.** 184, 1901; J. E. Stead, *ib.*, **14.** 444, 1895; Rieckher, *Zeit. anal. Chem.*, **9.** 516, 1870; J. A. Kaiser, *ib.*, **14.** 250, 1875; H. Beckurts, *Arch. Pharm.*, **222.** 653, 1884; A. Kleine, *Stahl Eisen*. **24.** 248, 1894; J. Clark, *Journ. Anal. App. Chem.*, **6.** 277, 1892; E. Ruff and F. Lehmann, *Arch. Pharm.*, **250.** 382, 1912; H. Hagen (*Pharm. Centr.* (3), **22.** 169, 1882) claims that the use of ferrous sulphate is due to himself and not to Fischer.

[3] Ferrous chloride, ferrous sulphate, ferrous ammonium sulphate (Classen and Ludwig), or cuprous oxide may be used. The presence of large quantities of the ferrous salt seems to prevent the well-known volatilisation of mercuric chloride with water vapour. Oxidising agents—nitric acid—should be absent, since they will oxidise the ferrous salt and make it inert. If present, nitric acid should be removed by evaporation with sulphuric acid. A little sulphuric acid does no harm. O. Piloty and A. Stock (*Ber.*, **30.** 1649, 1897; G. T. Morgan, *Journ. Chem. Soc.*, **85.** 1001, 1904) reduce by passing a stream of hydrogen sulphide through the boiling solution. If the arsenic be all present as arsenious salt, the ferrous salt is not needed. F. A. Gooch and E. W. Danner (*Amer. J. Science* (3), **42.** 308, 1891; F. A. Gooch and B. Hodge, *Zeit. anorg. Chem.*, **6.** 268, 1894; *Chem. News*, **70.** 23, 1894) reduce by means of potassium iodide and hydrochloric acid: F. A. Gooch and M. A. Phelps (*Zeit. anorg. Chem.*, **7.** 123, 1894) used potassium bromide and hydrochloric acid; M. Rohmer (*Ber.*, **34.** 33, 1565, 1901) reduced with sulphur dioxide, and H. B. Bishop (*Journ. Amer. Chem. Soc.*, **28.** 178, 1906) passed sulphur dioxide through the solution during the distillation and omitted the ferrous salt. This process gives good results, and can be used when the presence of iron is objectionable. C. Friedheim and P. Michaelis (*Ber.*, **28.** 1414, 1895; H. Cantoni and J. Chautems, *Archiv Sci. Phys. Nat. Genève* (4), **19.** 364, 1905; L. Moser and F. Perjatel, *Monats. Chem.*, **33.** 779, 1912; S. W. Collins, *Analyst*, **37.** 229, 1912) reduce with methyl alcohol; P. Jannasch and T. Seidel (*Ber.*, **43.** 1218, 1910; P. Jannasch and E. Heimann, *Journ. prakt. Chem.* (2), **74.** 437, 1906) reduce with 3 grms. of hydrazine sulphate, or hydrochloride, with excellent results. The time required is about an hour. This process can be recommended when the presence of iron is objectionable, and the hydrazine salt is available. M. Hoffmann (*Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 15, 1911) used potassium iodide with a current of hydrogen chloride gas.

[4] F. Wöhler, *Die Mineral-Analyse in Beispeilen*, Göttingen, 223, 1861.

Oxidation of Arsenious to Arsenic Salts.—The mixed sulphides obtained in the preceding operation are transferred to a beaker. Add, say, 2 to 3 grms. of potassium chlorate, and pour in *cautiously* 40 c.c. of dilute hydrochloric acid (30 c.c. of concentrated acid, 10 c.c. water). Cover the beaker with a clock-glass, and heat the mixture on a water bath until decomposition is complete, and all the chlorine oxides have been expelled. The object of the oxidation is to transform the arsenious salts to arsenic salts. The former are volatile with steam, while arsenic acid is not volatile.

Preparation for the Distillation.—Transfer the contents of the beaker to a 500–600 c.c. distillation flask. Wash the beaker with concentrated hydrochloric acid. Add, say, 25 grms. of ferrous ammonium sulphate and make the solution up to about 200 c.c. with concentrated hydrochloric acid.[1] Incline the flask at an angle of about 45°–60°, as illustrated in the diagram, fig. 125. Connect this flask with an Erlenmeyer's flask (3 or 4 litres) containing about a litre of concentrated fuming hydrochloric acid, saturated with sodium or ammonium chloride.[2] This flask is fitted with a delivery tube and a dropping funnel containing concentrated sulphuric acid. When the latter is dropped into the hydrochloric acid, hydrogen chloride is given off. The rate of evolution of the gas is determined by the rate at which sulphuric acid is dropped from the funnel. The neck of the distillation flask is connected with a condenser which has a tube dipping into water in a receiver (200 c.c.).[3] The receiver is

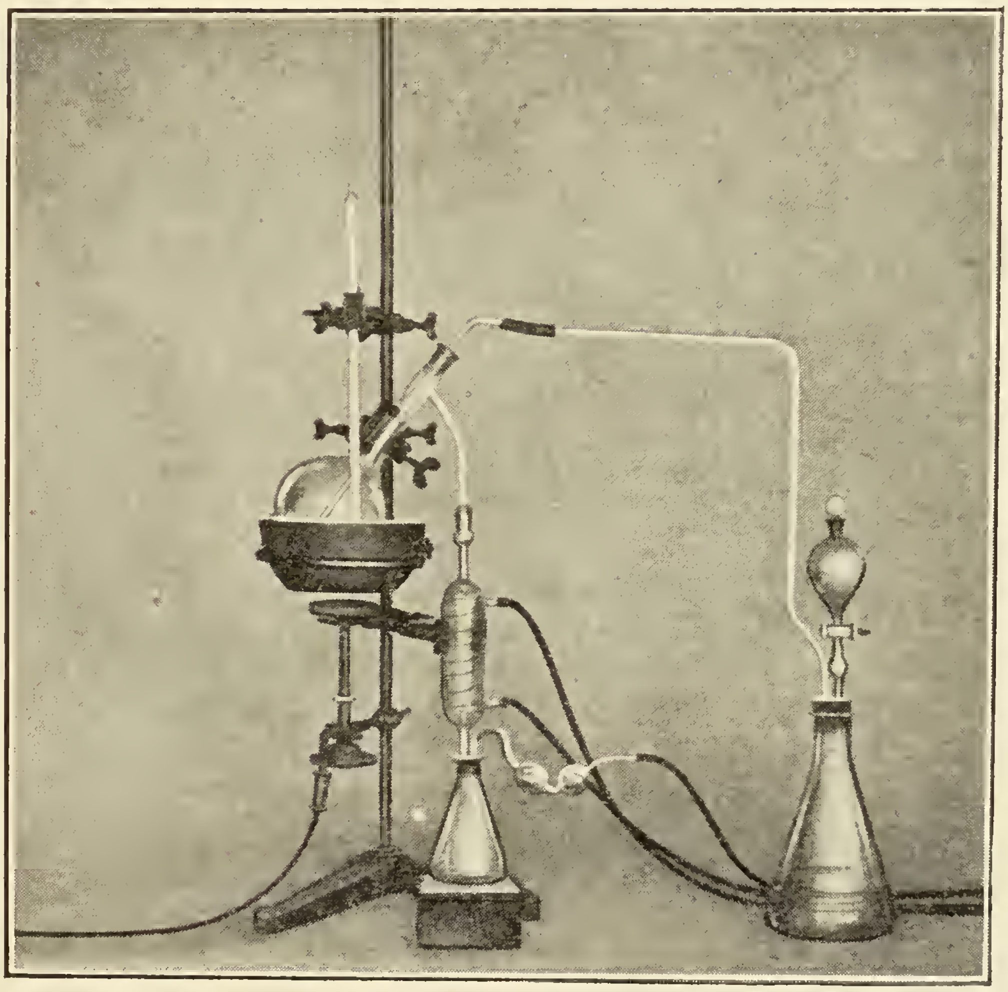

FIG. 125.—Apparatus for the separation of arsenic by distillation.

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[1] If antimony is to be afterwards determined by the distillation process (page 282), add 50 c.c. of a solution of zinc chloride made by saturating concentrated hydrochloric acid with metallic zinc, and evaporating till the solution boils at 108°.

[2] L. L. de Koninck (*Zeit. anal. Chem.*, 19. 467, 1880) uses concentrated sulphuric acid and solid ammonium chloride in a small gas generator—say Kipp's apparatus.

[3] L. Brandt (*Chem. Ztg.*, 33. 1114, 1909) condemns the use of a condensing apparatus, but advocates a delivery tube with a bulb, and drawn to a narrow point, and dipping into water in a beaker. The beaker is kept cool by being placed in a larger beaker containing cold water.

fitted[1] with a bulb tube to act as a water seal in case any chloride escapes condensation. If the condenser be adequately cooled, this will not be needed. The exit of the water seal must be directed outside the room.

The Distillation.—A slow current of hydrogen chloride[2] is passed through the apparatus for about an hour, so as to saturate the cold solution in the flask. The flask is then heated to boiling over an asbestos pad, or in an oil bath with a thermometer. The distillation is allowed to proceed while a rapid current of hydrogen chloride is passed through the system. A temperature of 108°–110° is best.[3] When about 80 c.c. have collected in the receiver, the distillation is stopped. A current of cold water is passed through the condenser all the time the distillation is in progress.

Determination of Arsenic in the Distillate.—The arsenic is best determined in the distillate by the volumetric process of Mohr[4] or Pearce. The arsenic may also be precipated by diluting the solution with hot water and saturating the boiling solution with hydrogen sulphide,[5] and it can be weighed in the form of arsenic trisulphide, silver arseniate, or magnesium pyrophosphate. The magnesium pyrophosphate process is described in the next section. If the arsenic is weighed as trisulphide, the precipitate from the hydrogen sulphide treatment is prepared as described for antimony trisulphide on page 296. The antimony and tin may be determined in the residue in the flask by precipitating the mixed sulphides of tin and antimony with hydrogen sulphide, and separating these two elements as indicated on page 305.[6]

This method gives excellent results. It occupies between two and three hours. The main objections are: (1) the need for a special apparatus; and (2) the consumption of time. If this process be inconvenient, the arsenic may be separated from the antimony and tin as ammonium magnesium arsenate.

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[1] All rubber tubing and stoppers should have been previously boiled with dilute potash to get rid of the sulphur.

[2] It is important to saturate the solution in the flask with hydrogen chloride before commencing the distillation. Fischer simply distilled from concentrated hydrochloric acid without keeping the solution saturated with a current of hydrogen chloride. This, however, renders repeated distillation necessary. One addition of hydrochloric acid, by Fischer's process, suffices for 0·01 grm. arsenic, but four distillations are needed for 1 grm., and the arsenic is not completely distilled off after the tenth distillation. With the current of hydrogen chloride, however, one distillation suffices for 0·5 grm. arsenious oxide. After 50 c.c. have passed over, no more arsenic can usually be detected in the distillate. The addition of calcium chloride to the solution in the flask gives better results in distilling from concentrated hydrochloric acid without passing hydrogen chloride through the system. This method may be used for small amounts of arsenic. For the action of hydrochloric acid on arsenic, see R. Fresenius, *Zeit. anal. Chem.*, **1.** 448, 1862.

[3] If the temperature of distillation exceeds 125°, some antimony, if present, will be found in the distillate—F. Platten, *Journ. Soc. Chem. Ind.*, **13.** 324, 1894.

[4] If the solution has to stand any length of time, and Mohr's process is intended, the solution should be nearly neutralised with sodium hydroxide and an excess of sodium bicarbonate added. This retards the rate of oxidation of the solution of arsenious chloride.

[5] H. Rose, *Handbuch der analytischen Chemie*, Berlin, 343, 1829; 390, 1871; R. E. O. Puller, *Zeit. anal. Chem.*, **10.** 45, 1871; C. Friedheim and P. Michaelis, *ib.*, **34.** 505, 1895; R. Bunsen, *Liebig's Ann.*, **192.** 305, 1878.

[6] Antimony can be separated by distillation, after the arsenic, by raising the temperature of the distillation flask up to 180°. The distillation of the antimony chloride commences about 125°. Under ordinary conditions, the contents of the distillation flask would become dry, and the antimony chloride would sublime on to the neck of the flask. It is therefore necessary to use a mixture in the retort which is not liable to evaporate to dryness, and which does not decompose under the conditions of the experiment. A. Gibb uses a solution of zinc chloride (page 280). After the distillation of the arsenic chloride, let the flask cool, change the receiver, and add 20 c.c. of concentrated hydrochloric acid. Fit up the apparatus as before, and gradually raise the temperature up to 200°, still maintaining the rapid current of hydrogen chloride. The antimony chloride will collect in the receiver. The antimony may be determined volumetrically by titration exactly as described for arsenic. The solution in the retort may be dissolved in hot water, and the tin determined as described below. There may be a loss of stannous chloride by this process if tin be present (L. A. Youtz, *Zeit. anorg. Chem.*, **35.** 55, 1903; W. Plato, *ib.*, **68.** 26, 1910).

§ 129. The Separation of Arsenic from Antimony and Tin as Magnesium Ammonium Arsenate.

Theoretical.—In 1846 Levol[1] showed that a precipitate of magnesium ammonium arsenate, resembling magnesium ammonium phosphate (page 215), is obtained when a magnesium salt is added to an ammoniacal solution of an arsenate. The precipitate so obtained is slightly soluble in water—100 grms. of water dissolve 0·036 grms. of $MgNH_4AsO_4$. The magnesium ammonium arsenate is hydrolysed by hot water forming "free arsenic acid, ammonium arsenate, and magnesia": $MgNH_4AsO_4 + 2H_2O = Mg(OH)_2 + NH_4H_2AsO_4$. If an aqueous solution be evaporated to dryness and the residue calcined, some arsenic is volatilised. "In the cold, magnesium ammonium arsenate is not hydrolysed by water."

The precipitate is much less soluble in ammoniacal solutions. A 2·5 per cent. solution of ammonia dissolves 0·0063 grm. of the salt per 100 grms. of the solvent. In consequence, it is usual to make the precipitation in ammoniacal solution. The presence of ammonium chloride augments the solubility of the precipitate. Thus, 100 grms. of a 1·41 per cent. solution of ammonium chloride dissolve 0·0735 grm. of the anhydrous $MgNH_4AsO_4$, while 100 grms. of a 12·5 per cent. solution dissolve 0·113 grm. of the salt. The presence of ammonium tartrate increases the solubility of the salt. Thus, 100 grms. of a 1·5 per cent. solution of tartaric acid, feebly ammoniacal, dissolves 0·07 grm. of $MgNH_4AsO_4$. The ammonium tartrate is required when the precipitation is made in the presence of tin and antimony salts. The solubility of the precipitate is also much reduced in alcoholic solution, and consequently many prefer to make the precipitation in a solution containing both alcohol and ammonia. The precipitate is fairly soluble in acids.

To find what amount of arsenic escaped precipitation, Hoffmann[2] determined the arsenic in the filtrate after application of the method described below. Starting with solutions containing the equivalent of 0·3 grm. of tin, 0·3 grm. of antimony, and

As (used) . . .	0·05	0·05	0·15	0·15	0·3	0·3	grm.
As in filtrate . . .	0·0006	0·0005	0·0008	0·0012	0·0006	0·0008	grm.

Traces only of tin and antimony were found in the precipitated magnesium ammonium arsenate. Fresenius proposed a correction for the unprecipitated magnesium arsenate—1 mgrm. arsenic per 30 c.c. of fluid. Dacru considers Fresenius' correction too small, and Virgili considers it too high. The latter recommended an allowance of 0·0012 grm. of arsenic per 100 c.c. of fluid, and this agrees best with Hoffmann's work.

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[1] A. Levol, *Ann. Chim. Phys.* (3), **17**. 501, 1846 ; *Compt. Rend.*, **23**. 57, 1846 ; W. Hampe, *Chem. Ztg.*, **18**. 1900, 1894 ; J. F. Virgili, *Zeit. anal. Chem.*, **44**. 492, 1905 ; R. Fresenius, *ib.*, **3**. 206, 1864 ; G. C. Wittstein, *ib.*, **2**. 19, 1863 ; R. E. O. Puller, *ib.*, **10**. 63, 1871 ; H. Lesser, *ib.*, **27**. 218, 1888 ; R. Brauner, *ib.*, **16**. 57, 1877 ; L. F. Wood, *ib.*, **14**. 356, 1875 ; *Amer. J. Science* (3), **6**. 368, 1893 ; F. A. Gooch and M. A. Phelps, *ib.* (4), **22**. 488, 1906 ; F. Reichel, *Zeit. anal. Chem.*, **20**. 89, 1881 ; C. Friedheim and P. Michaelis, *ib.*, **34**. 505, 1895 ; *Ber.*, **28**. 1414, 1895 ; R. Bunsen, *Liebig's Ann.*, **192** 305, 1878 ; C. Ullgren, *ib.*, **69**. 364, 1849 ; M. A. von Reis, *Stahl Eisen*, **9**. 270, 1885 ; H. Rose, *Pogg. Ann.*, **76**. 534, 1849 ; E. Raffa, *Gaz. Chim. Ital.*, **39**. i, 154, 1909 ; J. C. Brünnich and F. Smith, *Zeit. anorg. Chem.*, 68. 292, 1910.

[2] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 1911.

Magnesium ammonium arsenate is a white crystalline solid. Its composition corresponds with $MgNH_4AsO_4 . 6H_2O$ when dried over sulphuric acid in a desiccator, and $MgNH_4AsO_4 . \frac{1}{2}H_2O$ when dried at 100° on a water bath. When dried at higher temperatures, more water and possibly some ammonia are lost. On account of the indefinite character of the hydrated salt, it is not advisable to attempt to use this substance for the final weighing, as recommended by Koehler.[1] On ignition, the salt loses ammonia and water, forming magnesium pyroarsenate—$Mg_2As_2O_7$. If the ignition be conducted at too high a temperature, the magnesium pyroarsenate appears to decompose, and some arsenic oxide is volatilised. For instance, Friedheim and Michaelis[2] found that a precipitate which theoretically should have been 0·3621 grm. $Mg_2As_2O_7$ changed in weight on ignition as indicated in the following table:—

Table XLVI.—Influence of Calcination on Magnesium Pyroarsenate.

Burner.	Time of heating. Min.	Weight. Grms.
Bunsen's . .	30	0·3612
,, . .	60	0·3611
Blast . .	30	0·3602
,, . .	55	0·3596
,, . .	85	0·3587
,, . .	125	0·3576
,, . .	155	0·3572

There is thus a loss of 4 milligrams on blasting. The numbers also show that 30 minutes' calcination on a good Bunsen's burner is sufficient.

The Determination.—The solution of the freshly precipitated sulphides in sodium sulphide is evaporated nearly to dryness, and the residue digested with hydrochloric acid and potassium chlorate in a flask with a reflux condenser (page 303), in order to prevent loss by the volatilisation of arsenic chloride.[3] The solution should occupy about 100 c.c. Add (say, 12 grms.) tartaric acid,[4] ammonium chloride (about 2 grms. per 50 c.c.), and an excess of concentrated ammonia (one-third the total volume of the solution).[5] The arsenic is then precipitated from the clear ammoniacal solution by adding magnesia mixture (page 283) drop by drop with constant stirring. The volume of the magnesia mixture to be added is approximately one-third the total volume of the solution.[1] Let the mixture stand in a cool place for about 12 hours. Decant the clear liquid through a Gooch's crucible packed with asbestos. Wash with dilute ammonia water (2·5 per cent. of ammonia), first by decantation, and finally transfer the precipitate to the crucible.[2] Note the volume of filtrate and washings. Dry the precipitate at about 109°. Place a crystal of ammonium nitrate in the crucible,[3] and gradually raise the temperature until the saucer containing the Gooch's crucible (page 106) is bright red. Too high a temperature is bad, since some arsenic may be lost. Cool in a desiccator and weigh as $Mg_2As_2O_7$.[4] The weight of the magnesium pyroarsenate multiplied by 0·6374 represents the corresponding amount of As_2O_3.

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[1] O. Koehler, *Archiv Pharm.* (3), **27**. 406, 1889.

[2] E. W. Parnel, *Chem. News*, **21**. 133, 213, 1870; R. W. E. Macivor, *ib.*, **32**. 283, 1875; F. Field, *ib.*, **21**. 193, 1870; *Journ. Chem. Soc.*, **26**. 6, 1873; C. Rammelsberg, *Ber.*, **7**. 544, 1874; L. Chevron and A. Droixhe, *Bull. Acad. Belg.* (3), **16**. 475, 1888; F. Reichel, *Zeit. anal. Chem.*, **20**. 89, 1881; R. Brauner, *ib.*, **16**. 57, 1877; C. Friedheim and P. Michaelis, *ib.*, **34**. 505, 1895; M. Austin, *Zeit. anorg. Chem.*, **23**. 146, 1900; C. Lefèvre, *Ann. Chim. Phys.* (6), **27**. 55, 1892.

[3] O. Piloty and A. Stock, *Ber.*, **30**. 1649, 1897.

[4] The object of the tartaric acid is to keep the tin and antimony in solution. If much tin be present, the addition of ammonia may produce a turbidity, showing that insufficient tartaric acid is present. In that case, decant off the clear, dissolve the precipitate in tartaric acid on a water bath, and then mix the solutions (page 295).

[5] Some recommend the addition of one-third the volume of 95 per cent. alcohol at this stage. F. Field, *Journ. Chem. Soc.*, **26**. 6, 1873; R. E. O. Puller, *Zeit. anal. Chem.*, **10**. 57, 1871; C. R. Fresenius, *ib.*, **3**. 206, 1864; F. Reichel, *ib.*, **20**. 89, 1881; C. Friedheim and P. Michaelis, *ib.*, **34**. 505, 1895; H. Rose, *ib.*, **1**. 417, 1862; *Pogg. Ann.*, **76**. 534, 1849; L. F. Wood, *Amer. J. Science* (3), **6**. 368, 1873; M. Austin, *ib.* (4), **9**. 55, 1900; O. C. Beck and H. Fisher, *Chem. News*, **80**. 259, 1899; *School Mines Quart.*, **20**. 372, 1899.

Except for the disadvantage which attends the slow precipitation, especially when two precipitations are made, the method is quite satisfactory. A correction of 0·0016 grm. of As_2O_3 per 100 c.c. of filtrate and washings may be allowed.

EXAMPLE.—Suppose the precipitate has been in contact with approximately 150 c.c. of liquid, and

Crucible and precipitate	10·31428 grm.
Crucible	10·0014 grm.
$Mg_2As_2O_7$	0·3128 grm.

Hence 0·3128 × 0·6373 = 0·1993 grm. As_2O_3. Since 100 c.c. of filtrate involves a correction of + 0 0016 grm., we have 0·1993 + 0·0024 = 0·2017 grm. of As_2O_3 in the given sample, which weighed 5 grms. Hence the sample has the equivalent of 4·03 per cent. As_2O_3.

Comparison Determinations.—In a separation of arsenic from mixed tin and antimony sulphides by the distillation process, and the arsenic subsequently determined by this and the two processes described below, the percentage arsenic obtained was:

Levol's process.	Mohr's process.	Pearce's process.
8·25	8·25	8·15
8·30	8·29	8·19

Distillation process of separation.

The filtrate is just acidified with hydrochloric acid and saturated with hydrogen sulphide, whereby the sulphides of tin and antimony are precipitated as indicated on page 276 ; or the solution may be divided into two parts, and the antimony and tin determined separately, as indicated on page 305.[5]

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[1] The precipitation is facilitated by the addition of a little alcohol—E. Murmann, *Oester. Chem. Ztg.*, **13**. 227, 1910.

[2] Some filter here through filter paper, and dissolve the precipitate in hydrochloric acid. The magnesium arsenate is reprecipitated in order to eliminate a possible contamination of the first precipitate with magnesia, more particularly if magnesium sulphate is one of the components of the magnesia mixture.

[3] Or ignite in a current of oxygen in a Rose's crucible.

[4] If filter paper be employed, some arsenic may be lost by volatilisation. Destruction of the filter paper by nitric acid gives good results—L. L. de Koninck (*Zeit. anal. Chem.*, **29**. 165, 1890). W. Hampe prefers to dissolve the precipitate in hydrochloric acid, remove the arsenic by passing hydrogen sulphide, and determine the magnesia in the filtrate by precipitating as magnesium phosphate (page 218). A better plan is to determine the arsenic volumetrically by dissolving the precipitated magnesium ammonium arsenate in acid and proceeding as indicated for Mohr's process, or Pearce's process.

[5] It will be remembered that many kinds of glass, as well as caustic alkalies, contain arsenic (page 184), but not in quantities likely to affect quantitative results by the processes here described—R. Fresenius, *Zeit. anal. Chem.*, **6**. 201, 1867 ; W. Fresenius, *ib.*, **22**. 397, 1883 ; J. Marshall and C. Pott, *Amer. Chem. Journ.*, **10**. 425, 1888 ; S. R. Scholes, *Journ. Ind. Eng. Chem.*, **4**. 16, 1912.

§ 130. Notes on Iodine, Potassium Iodide, Starch, and Sodium Thiosulphate.

In 1853, Bunsen[1] demonstrated the general applicability of reactions in which iodine was liberated from potassium iodide for volumetric analysis. Bunsen used sulphurous acid for measuring the iodine set free. Schwarz[2] used sodium thiosulphate for titrating iodine in neutral or acid solutions, and Mohr extended the process to solutions of arsenious and antimonious salts in alkali carbonate solutions. F. Stromeyer first used starch for developing the tint of free iodine.[3] Starch, iodine, potassium iodide, and sodium thiosulphate are now used so frequently in certain types of volumetric work, that some notes on the use of these substances may now be made.

Starch Solutions.

Starch is used as an indicator in titrations with iodine solutions. Free iodine colours an aqueous solution of starch blue only in the presence of a soluble iodide. The sensitiveness of the reaction is determined by the composition of the solution. Sodium sulphate makes the reaction very sensitive, *e.g.*, a $\frac{1}{5}$N-solution of sodium sulphate (with starch) gives a colour with a 0·0000017N-iodine solution.[4] Some believe the blue substance is a solid solution,[5] while others consider it to be a compound of hydriodic acid with an iodine addition product of starch[6]—$C_{24}H_{40}O_{20}I_4 . HI$. The addition product—$C_{24}H_{40}O_{20}I_4$—is supposed to be colourless in aqueous solution. It is further supposed that the blue compound $C_{24}H_{40}O_{20}I_4 . KI$ is dissociated in dilute aqueous solutions into colourless $C_{24}H_{40}O_{20}I_4$ and KI. When the concentration of the latter is increased, the concentration of the blue $C_{24}H_{40}O_{20}I_4 . KI$ is increased, and the solution appears blue. This latter hypothesis agrees best with the facts.

One gram of potato (arrowroot, corn, or rice) starch is triturated with 10 c.c. of cold water until a smooth paste is obtained. Add sufficient boiling water with constant stirring to make 200 c.c. of a thin translucent fluid. If the fluid be not transparent, it must be boiled two or three minutes, but prolonged boiling must be avoided, since it converts some of the starch into dextrine. Cool the solution. Let it settle overnight, and decant off the clear. This solution will not keep more than a couple of days. A larger quantity can be made and the clear liquid poured into small 50-c.c. phials up to the neck. The phials are placed in a water bath, heated for a couple of hours, and then closed by cork stoppers. The solution so preserved will keep indefinitely. When a phial is opened, the contents deteriorate in a few days, hence the use of small bottles, which permits the solution to be used before it spoils. In order to prevent deterioration, preservatives are frequently added, *e.g.*, a few drops of chloroform, oil of cassia, salicylic acid, zinc chloride, zinc iodide, or mercuric chloride (2 grms. per litre of paste).[7]

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[1] R. Bunsen, *Liebig's Ann.*, 86. 265, 1853.

[2] C. L. H. Schwarz, *Praktische Anleitung zu Maassanalysen*, Braunschweig, 1853.

[3] F. Stromeyer, *Schweigger's Journ.*, 12. 349, 1814.

[4] J. Pinnow, *Zeit. anal. Chem.*, 41. 485, 1902; C. Meineke, *Chem. Ztg.*, 18. 157, 1894; A. Eckstadt, *Zeit. anorg. Chem.*, 29. 51, 1901.

[5] F. W. Küster, *Liebig's Ann.*, 283. 360, 1895.

[6] F. Mylius, *Ber.*, 20. 688, 1881; C. Lonner, *Zeit. anal Chem.*, 33. 409, 1894; L. W. Andrews and H. M. Goettsch, *Journ. Amer. Chem. Soc.*, 24. 865, 1902; H. B. Stocks, *Chem. News*, 56. 212, 1887.

[7] G. Gastine, *Bull. Soc. Chim.* (2), 50. 172, 1888; M. Musculas, *Compt. Rend.*, 78. 1483, 1874; M. Mütnianski, *Zeit. anal. Chem.*, 36. 220, 1897; C. Reinhardt, *ib.*, 25. 37, 1886; F. Mohr, *ib.*, 14. 79, 1875; A. Müller, *ib.*, 22. 76, 1883; A. Wroblewski, *Journ. Pharm. Chim.* (6), 8. 314, 1907; O. Förster, *Chem. Ztg.*, 21. 41, 1897; L. Mathieu, *Bull. Assoc. Chem. Sucr. Dist.*, 27. 1166, 1910.

Zulkowsky's[1] soluble starch is very convenient for titrations. It is sold in the form of a thick paste. A small portion is taken from the stoppered bottle on the end of a clean glass rod, and then mixed with water in a test-tube for use. The so-called "soluble starch" is made by grinding, say, 100 grms. of rice starch with a 2 per cent. potash solution until a homogeneous solution is obtained. Stir the solution with more potash, so that the volume of the mixture is from 600 to 800 c.c. Heat the mixture on a water bath until all is quite liquefied, and then 30 to 40 minutes over a free flame. Filter. Add an excess of acetic acid to the filtrate. Finally precipitate the starch by adding an equal volume of 95 per cent. alcohol. Redissolve the precipitate, again precipitate the starch, and dissolve the precipitate in the least possible quantity of water. Pour the solution in a thin stream into a large quantity of absolute alcohol. Filter the precipitate and wash the precipitate with alcohol, and finally with ether. Dry *in vacuo*. The yield is about 50 or 60 per cent. "Soluble starch" is a commercial article. It is sold as a white powder, which dissolves readily in boiling water, forming a clear solution. The reaction of iodine with these purified starches is sensitive and sharp.

If impure starch be used for the work, a loss of iodine may occur owing to the presence of erythrodextrine, which gives a reddish colour with iodine.[2] If a preservative has been used with the starch, it may be necessary to be prepared for certain disturbances, *e.g.*, the presence of zinc chloride would interfere in the titration of sulphides and carbonates. In using starch as an indicator with iodine titrations, if nitrogen fumes are in the atmosphere of the laboratory, a rapid "after-blueing" of the solution may lead to high results.[3]

Potassium Iodide.

The potassium iodide used in volumetric work must be free from iodates. To test if the potassium iodide is suitable for the work, dissolve a gram of the salt in 11 c.c. of water, and add a drop of pure hydrochloric acid. If iodates be present, free iodine will be formed:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O.$$

Shake the mixture with a little chloroform. If the chloroform shows no coloration, or, at the worst, a faint tint, the potassium iodide is suitable for the work,[4] and sufficiently free from contamination with substances which decompose potassium iodide.

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[1] K. Zulkowsky, *Ber.*, 13. 1395, 1874.

[2] F. E. Hale, *Amer. J. Science* (4), 13. 379, 1902; C. Lonnes, *Zeit. anal. Chem.*, 33. 409, 1894; C. Meineke, *Chem. Ztg.*, 18. 157, 1894; 19. 5, 1895; G. Rivat, *Chem. Ztg.*, 34. 1141, 1910; L. Mathieu, *Ann. Chim. Anal.*, 16. 51, 1911.

[3] F. Sinnatt (*Analyst*, 35. 309, 1910; 37. 252, 1912) recommends methylene blue in place of starch in titrating with standard iodine solutions. 0·05 grm. of the dye is dissolved in water, and the solution made up to 50 c.c. One c.c. of this solution per 50 c.c. of the solution to be titrated is used as indicator. The end point is indicated by a change from blue to yellowish green. It might here be added that B. Schwezoff (*Zeit. anal. Chem.*, 44. 85, 1905) and A. Bobierre (*Monit. Scient.* (2), 5. 951, 1868; *Chem. News*, 18. 265, 1868) substitute for the starch reaction with iodine the intense red coloration furnished by the solution of iodine in colourless benzene, a reaction suggested by M. Moride in 1852 (*Compt. Rend.*, 35. 789, 1852; B. M. Margosches, *Zeit. anal. Chem.*, 44. 392, 1905). M. Bertin (*Journ. de Médecine de l'Ouest*, 31. 201, 1868) also used the same reaction. A. Dupré (*Ann. Chim. Pharm.*, 94. 365, 1855) used chloroform, which is less convenient than benzene. It is claimed that the benzene reaction is 2½ times as sensitive as starch. E. Borgmann (*Nederl. Tijdschr. Pharm.*, 8. 140, 1896) used an alcoholic solution of kakotelin.

[4] F. Pollaci, *Gaz. Chim. Ital.*, 3. 474, 1873. This test is often prescribed for iodates, but traces of iron or cuprous oxides, in the presence of dissolved oxygen, also give the pink colour. L. W. Andrews (*Journ. Amer. Chem. Soc.*, 31. 1035, 1909) detects iodates by using potassium hydrogen tartrate in place of hydrochloric acid.

Iodine.

Iodine—I. Atomic and equivalent weights: 126·92.

The most commonly employed solutions are:

	Grms. I per c.c.
$\frac{1}{10}$N-Iodine	0·012692
$\frac{1}{100}$N-Iodine	0 001269

Since iodine is but sparingly soluble in water, it is necessary to augment the solubility by using solutions of potassium iodide as a solvent for the iodine. Hence, dissolve 12·69 grms. of iodine and 18 grms. of potassium iodide in about 300 c.c. of water in a litre flask, and make the solution up to a litre. The solution is standardised by decinormal sodium thiosulphate, or by means of arsenious oxide.[1]

Commercial iodine may contain chlorine, bromine, water, cyanogen, etc. To purify iodine[2] on a large scale, dissolve 4 kilograms of iodine in a solution containing 2 kilograms of potassium iodide, dissolved in 2 litres of water. Pour the solution into water, and let it stand until the iodine is precipitated. The chlorine or bromine present react with the potassium iodide, liberating iodine and forming potassium chloride or bromide. Pour off the supernatant liquid; wash the iodine with water[3] until it is free from potassium iodide; filter through a layer of sand assisted by suction. Transfer the iodine to a shallow dish, and dry the mass over concentrated sulphuric acid (12 days). Place the iodine in a combustion tube slightly inclined, with a plug of asbestos placed so as to prevent the melted iodine running down the tube. The lower end of the combustion tube is connected with a couple of drying tubes, one containing calcium chloride, and the other phosphorus pentoxide, in order to dry the air which is to pass through. The upper end of the combustion tube is covered by a bottle fitted with a rubber stopper to catch any iodine vapours not previously condensed. The stopper is fitted with a glass tube connected with a cylinder, which acts as an aspirator. The suction is sufficient to enable the iodine to condense far enough from the heated portion to prevent liquefaction of the sublimed crystals. To prevent an accident from the sudden heating of the tube, place a piece of iron pipe over the part of the tube containing the asbestos and iodine, and extending about 10 cm. beyond the tube. A layer of asbestos is placed between the glass and iron tubes. This process is not convenient if but small quantities of iodine have to be treated.

To purify small quantities of iodine, grind, say, 6 grms. of commercial iodine with 2 grms. of potassium iodide. Put the dry mixture in a small dry beaker (fig. 126) fitted with a Göckel's condenser.[4] The beaker is surrounded with a cylindrical asbestos jacket (not shown in the diagram). Place the beaker on a wire gauze, or a hot plate, and heat the apparatus by means of a small flame.

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[1] See next section.

[2] L. L. de Koninck, *Bull. Assoc. Chim. Belg.*, **17**. 15, 1904; J. S. Stas, *Œuvres Complètes*, Bruxelles, **1**. 563, 1894; G. C. Wittstein, *Dingler's Journ.*, **200**. 310, 1871; C. F. Mohr, *Lehrbuch der chemisch-analytischen Titrirmethode*, Braunschweig, 269, 1874; A. Gross, *Journ. Amer. Chem. Soc.*, **25**. 987, 1903; *Chem. News*, **88**. 274, 1903; L. W. Andrews, *ib.*, **90**. 27, 1904; *Amer. Chem. Journ.*, **30**. 428, 1903; B. Lean and W. H. Whatmough, *Proc. Chem. Soc.*, **14**. 5, 1898; C. Meineke, *Chem. News*, **68**. 272, 1893; *Chem. Ztg*, **16**. 1219, 1230, 1892; Z. Musset, *Zeit. anal. Chem.*, **30**. 45, 1891; G. Lunge, *Zeit. angew. Chem.*, **7**. 234, 1894; A. Ladenburg, *Ber.*, **35**. 1256, 1902.

[3] The washings, particularly at first, are retained and the iodine recovered.

[4] H. Göckel, *Zeit. angew. Chem.*, **12**. 494, 1899.

The condenser is full of cold water, at the temperature of the room. When violet vapours have ceased to come from the bottom of the beaker, let the apparatus cool. A crust of iodine will be found on the condenser. Pass a current of cold water through the condenser. The glass contracts, and the crust of iodine can be easily removed by pushing it with a glass rod into a similar beaker. The sublimation is repeated without the potassium iodide at as low a temperature as possible. Grind the iodine in an agate mortar, and dry in a desiccator over calcium chloride, not sulphuric acid, or the iodine may be contaminated. If the cover of the desiccator is greased, the iodine may attack the grease, forming hydriodic acid, which might contaminate the iodine.

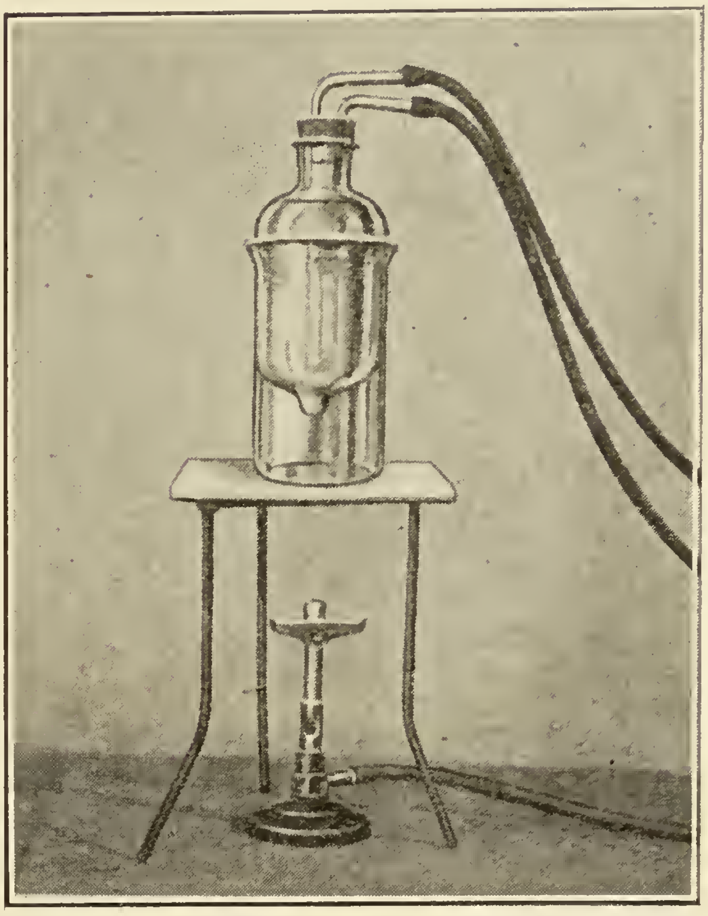

FIG. 126.—Purification of Iodine.

Preservation of Iodine Solutions.—Iodine solutions should only be kept in glass-stoppered bottles—preferably made of brown glass, to cut off the light. Iodine solutions diminish in strength with time, particularly if the bottle with the stock solution is frequently opened, owing to the volatilisation of the iodine. According to Schmatolla,[1] a $\frac{1}{10}$N-solution of iodine scarcely changes if kept for a year, particularly if the space between the stopper and the neck of the bottle be kept dry. The presence of an excess of potassium iodide lowers the vapour pressure of the iodine vapour and makes the solution keep better.

Sodium Thiosulphate.

Anhydrous sodium thiosulphate—$Na_2S_2O_3$; crystalline sodium thiosulphate—$Na_2S_2O_3.5H_2O$. Molecular weight of the crystalline salt: 248·22; equivalent weight: 248·22. Molecular weight of anhydrous salt: 158·14; equivalent weight: 158·14.

The most commonly employed solution has the strength:—

	Grms. per c.c.	
$\frac{1}{10}$N-Sodium thiosulphate	0·024822	(crystalline salt)
	0·015814	(anhydrous salt)

Sodium Thiosulphate.—This salt is much used in iodine titrations; the thiosulphate, in acid solutions,[2] is transformed by iodine into tetrathionate:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

The anhydrous sodium thiosulphate is made by recrystallising the "pure" commercial salt from warm solutions, saturated at 30°–35°, by cooling and constant stirring. The fine-grained crystals so obtained are dried on filter paper at the temperature of the room. The salt is then dehydrated over concentrated sulphuric acid until it has fallen to powder, and a portion heated in a test tube shows no signs of fusion when heated to 50°. The dehydration is completed at 80° in an air bath with repeated stirring of the powder. For relatively small quantities, two hours will suffice. Preserve the salt in well-stoppered bottles. Young[1] finds that the salt so prepared keeps well and may be itself used for standardising iodine solutions.

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[1] O. Schmatolla, *Apoth. Ztg.*, 17. 248, 1902.

[2] In alkali or sodium hydrogen carbonate solutions, sodium thiosulphate and tetrathionate are partly oxidised to sulphate.—G. Topf, *Zeit. anal. Chem.*, 26. 137, 277, 1887; J. P. Batey, *Analyst*, 36. 132, 1911; E. Abel, *Zeit. anorg. Chem.*, 74. 395, 1912; C. Friedheim, *Zeit. angew. Chem.*, 4. 415, 1891.

The molecular weight of the crystalline salt—$Na_2S_2O_3 . 5H_2O$—is 248·22; and of the anhydrous salt—$Na_2S_2O_3$—158·14. For a litre of the normal solution, one molecular weight of the salt expressed in grams is employed. The solutions should be made with water free from carbon dioxide, since the latter reacts with the thiosulphate, forming sodium sulphite and free sulphur:

$$Na_2S_2O_3 + 2H_2CO_3 \rightarrow Na_2SO_3 + H_2O + 2CO_2 + S.$$

The sodium sulphite reacts with more iodine than the corresponding thiosulphate, and hence the solution appears to become more concentrated on standing. After all the carbon dioxide in the water has reacted with the thiosulphate, the solution may be kept for months without appreciable change.[2] Treadwell found no change in the titre of a solution against iodine after it had been kept for eight months. The addition of ammonium carbonate, sometimes recommended to preserve the solution, really acts in the opposite direction, and makes the solution less stable.[3]

§ 131. Mohr's Iodine Volumetric Process for Arsenic.

Theoretical.—When a solution of iodine is gradually added to a solution containing arsenious oxide, the latter is oxidised[4] to arsenic oxide, and a colourless solution of hydriodic acid is formed:

$$As_2O_3 + 2H_2O + 2I_2 = 4HI + As_2O_5.$$

When all the arsenious oxide has been oxidised, any further addition of iodine produces a yellow colour, or, if a solution of starch be present, blue starch iodide is formed. The starch solution enables one part of iodine in over three million parts of the solution to be detected. It is best to work with cold solutions, since the starch iodide dissociates on heating and loses its blue colour. The blue colour re-forms on cooling.

The solution should be alkaline in order to neutralise the hydriodic acid formed in the reaction. Alkaline hydroxides will not do, because they react with starch iodide, and with free iodine ($6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O$); sodium carbonate is partly hydrolysed[5] in aqueous solutions ($Na_2CO_3 + H_2O = NaOH + NaHCO_3$). It therefore reacts with iodine, but to a less extent than sodium hydroxide. For example, working with a solution of iodine (1 c.c. = 0·005 grm. iodine) and a saturated solution of sodium carbonate, Waitz found:

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[1] S. W. Young, *Journ. Amer. Chem. Soc.*, **26**. 1028, 1904; G. Topf, *Zeit. anal. Chem.*, **26**. 140, 1887.

[2] C. Meineke, *Chem. Ztg.*, **18**. 33, 1894; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 530, 534, 1911.

[3] See S. U. Pickering (*Chem. News*, **44**. 277, 1881) for the deterioration of sodium thiosulphate with keeping. The solution should be kept in amber-coloured small glass-stoppered bottles, carefully protected from dust, air, and light. It should be re-standardised frequently.

[4] E. Waitz, *Zeit. anal. Chem.*, **10**. 158, 1871; S. Avery and H. T. Beans, *Journ. Amer. Chem. Soc.*, **23**. 485, 1901; J. K. Haywood, *ib.*, **25**. 963, 1903; S. Avery, *ib.*, **25**. 1096, 1903; E. W. Washburn, *ib.*, **30**. 31, 1908; F. Mohr, *Lehrbuch der chemisch-analytischen Titrirmethode*, Braunschweig, 1859; J. P. Batey, *Analyst*, **36**. 132, 1911; B. E. Curry and T. O. Smith, *Journ. Ind. Eng. Chem.*, **4**. 198, 1912; G. S. Jamieson, *ib.*, **3**. 250, 1911.

[5] H. N. M'Coy, *Amer. Chem. Journ.*, **24**. 437, 1900.

Water . . .	20	20	50	20	100	c.c.
Sod. carb. solution .	5	10	10	20	20	c.c.
Iodine sol. required .	0·25	0·3	0·35	0·8	1·1	c.c.

It is generally supposed that sodium bicarbonate does not react with iodine, and Beringer[1] quotes the following experiment to show that "a large variation in the quantity of bicarbonate has no effect" on the consumption of iodine:

Sodium bicarbonate . .	1	2	5	10	grms.
Iodine solution required .	20·1	20·0	20·1	20·0	c.c.

The truth is that the sodium bicarbonate is slightly hydrolysed in aqueous solutions, forming sodium carbonate and carbonic acid ($2NaHCO_3 = Na_2CO_3 + H_2CO_3$). The sodium carbonate is further hydrolysed, as indicated above. The amount hydrolysed is increased at elevated temperatures and in concentrated solutions.[2] Hence, in using sodium bicarbonate to neutralise the hydriodic acid, the solution should be as nearly neutral as possible at the *end* of the titration to get the best results. A deficiency of the sodium bicarbonate is very objectionable. A slight excess does no serious harm, since the results will be sufficiently exact for commercial work.[3] The solution to be titrated should be dilute and cold. The titration should also be performed as quickly as possible to avoid variations in the concentration of the acid in solution by the escape of carbon dioxide.

The Determination.—The acid solution of the arsenious compound[4] is nearly neutralized with ammonia or sodium hydroxide.[5] Add 20 c.c. of a saturated solution of sodium bicarbonate,[6] and 2 or 3 c.c. of a solution of starch, and titrate with standard iodine solution[7] until a permanent blue tinge remains suffused through the solution. The end point is very sharp, and consequently the iodine must be added very gradually towards the end of the titration.

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[1] C. and J. J. Beringer, *A Textbook of Assaying*, London, 387, 1908.

[2] W. A. Puekner (*Proc. Amer. Phil. Assoc.*, **43**. 408, 1904) considers the amount of hydrolysis is also slightly greater in large flasks than in small flasks owing to the escape of more carbon dioxide. The carbon dioxide is evolved during the titration by the decomposition of the carbonic acid ($H_2CO_3 = H_2O + CO_2$). Hence, the titration should be made in Erlenmeyer's flasks, not in beakers.

[3] The labour involved in the exact adjustment of the bicarbonate for "unknown" solutions might be considered "finicking" by a commercial analyst. Every 100 c.c. of $\frac{1}{10}$N-iodine solution needs about 5 grms. of sodium bicarbonate, on the assumption that the solution is neutral before adding this amount of sodium bicarbonate. E. W. Washburn (*Journ. Amer. Chem. Soc.*, **30**. 31, 1908) avoids the disturbances with sodium bicarbonate by using 11 grms. sodium phosphate—$Na_2HPO_4 . 12H_2O$—for every 100 c.c. of the $\frac{1}{10}$N-iodine solution. The sodium phosphate is supposed to be added to the neutral solution. For errors with an excess of sodium bicarbonate, see J. P. Batey, *Analyst*, **36**. 132, 1911; M. Bialobrzcsky (*Zeit. anal. Chem.*, **37**. 444, 1898) recommends ammonium acetate in place of sodium bicarbonate.

[4] If arsenic salts be present, the solution must be reduced by, say, a crystal of potassium iodide and an excess of sulphur dioxide. The sulphur dioxide destroys the free iodine. If all the sulphur dioxide be boiled off before the reduction is complete, the first drop of iodine from the burette in the titration will probably colour the solution yellow. If the reduction be complete, no permanent coloration will be produced when a crystal of potassium iodide is dropped into the solution. The solution must also be boiled free from sulphur dioxide (test for sulphur dioxide as indicated page 192). Avoid prolonged boiling (page 300).

[5] The ammonia should be free from pyrrol. This is readily obtained by tinging ammonia with potassium permanganate and afterwards decanting from the deposit formed.

[6] Free from nitrites, chlorates, etc.

[7] STANDARD IODINE SOLUTION.—Shake, say, 1·05 grms. of resublimed iodine along with 4 grms. of potassium iodide (free from iodates) with about 2 c.c. of water in a litre flask until the iodine is dissolved. This occupies but two or three minutes. Make the solution up to a litre. Standardise the solution of iodine by dissolving 0·4092 grm. of pure arsenious oxide in a hot solution containing about 20 grms. of sodium hydroxide (free from sulphur) in 100 c.c. of water (B. Penot, *Dingler's Journ.*, **127**. 134, 1853; L. Müller, *ib.*, **129**. 286, 1853; D. Hancoek, *Journ. Amer. Chem. Soc.*, **16**. 431, 1894); acidify the solution with hydrochloric acid, and then make

Example.—Suppose 1·5 grms. of material be under investigation and the solution requires 26·2 c.c. of iodine containing the equivalent of 0·0004092 grm. of As_2O_3 per cubic centimetre, then the material contains the equivalent of

$$\frac{0{\cdot}0004092 \times 26{\cdot}2 \times 100}{1{\cdot}5} = 0{\cdot}715 \text{ per cent. of } As_2O_3.$$

Correction for the Volume of the Liquid being titrated.—With the same amount of arsenic, and different volumes of liquid, different volumes of the standard iodine solution may be needed to develop the starch blue. Hence the solution to be titrated should have nearly the same concentration as the solution used for standardising the iodine. The error is not very marked with $\frac{1}{10}$N- and stronger iodine solutions, but with more dilute solutions, say $\frac{1}{100}$N-, the error is quite appreciable. *The more dilute the solution, the greater the amount of iodine needed to produce the coloration.* When the solution is less than 150 c.c. and potassium iodide is present, the same amount of the iodine solution is needed to produce the blue colour; but if the volume of the solution to be titrated be greater than 150 c.c., more iodine is necessary the greater the volume of the solution. Thus, Treadwell[1] found, with no other potassium iodide than that present in the standard solution:

Water	50	100	150	200	c.c.
$\frac{1}{100}$ N-Iodine	0·15	0·30	0·47	0·64	c.c.

In the presence of 1 grm. potassium iodide, Treadwell found:

Water . . .	50	100	150	200	500	c.c.
$\frac{1}{100}$N-Iodine . .	0·04	0·04	0·04	0·14	0·32	c.c.

If the solutions to be titrated vary in volume, it is therefore necessary to apply a correction for the amount of the standard solution required to produce a coloration after the reaction between iodine and arsenious oxide is completed (page 200).

§ 132. Pearce's Volumetric Process for Arsenic.

In Bennett's modification of Pearce's process,[2] the compound containing the arsenic is oxidised. The arsenic oxide is precipitated as silver arsenate. The silver in the silver arsenate is determined by Volhard's volumetric process, and the corresponding As_2O_3 is computed by rule of three. In the older process of E. Reich (1864), the silver arsenate is determined gravimetrically, and this may be advisable when standard solutions are not available, and only an occasional arsenic determination has to be made.[3]

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the solution alkaline with sodium bicarbonate; cool; make the solution up to a litre. Pipette 50 c.c. of this solution into a flask; add a couple of drops of starch solution, and titrate with the iodine solution until the permanent blue tinge is obtained. If 50 c.c. of the iodine solution are required, 1 c.c. of iodine solution represents 0·0004092 grm. of As_2O_3. The solution of iodine keeps very well if kept in a cool place in the dark.

[1] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2.** 536, 1911; Eng. trans., New York, **2.** 513, 1904.

[2] R. Pearce, *Proc. Colorado Scientific Soc.*, **1.** 14, 1883; *Chem. News*, **48.** 85, 1883; F. Reich, *Zeit. anal. Chem.*, **25.** 411, 1886; A. H. Low, *Journ. Amer. Chem. Soc.*, **28.** 1715, 1906; J. F. Bennett, *ib.*, **21.** 431, 1899; L. R. W. McCay, *Amer. Chem. Journ.*, **8.** 77, 1886; **12.** 547, 1890; *Chem. News*, **48.** 7, 168, 1883; O. J. Frost, *ib.*, **48.** 85, 1883; **53.** 221, 232, 243, 1886; T. Brown, *ib.*, **81.** 178, 184, 1900; *Journ. Amer. Chem. Soc.*, **21.** 1899; R. C. Canby, *Trans. Amer. Inst. Min. Eng.*, **17.** 77, 1888; G. W. Lehmann and W. Mager, *Amer. Chem. Journ.*, **7.** 112, 1885; H. E. Hooper, *Eng. Min. Journ.*, **94.** 706, 1912

[3] In that case, the silver arsenate is precipitated as described in the text, filtered and washed with a dilute solution of ammonium nitrate. The precipitate is dissolved in ammonia,

Precipitation of Silver Arsenate.—The arsenic compound is dissolved in nitric acid—warming the solution if necessary. This oxidises the arsenious to arsenic oxide.[1] Add a few drops of phenolphthalein to the cold solution, and add sodium hydroxide until the indicator turns pink. Then add acetic acid, drop by drop, with constant stirring until the colour is discharged,[2] and add one drop of dilute acetic acid [3] in excess.[4] The solution now occupies about 100 c.c. Add an excess, say, 10 c.c., of a neutral solution of silver nitrate[5] with vigorous stirring. Let the precipitate settle a few minutes; decant the clear; wash twice by decantation; and, finally, filter off the brick-red precipitate of silver arsenate—Ag_3AsO_4. Wash the precipitate with cold water until it is free from silver acetate and nitrate when tested with a drop of sodium chloride solution.

Titration for the Silver.—Dissolve the precipitate in 5–10 c.c. of dilute nitric acid (1 : 1), and collect the filtrate, washings, etc., in a beaker.[6] Dilute the solution, if necessary, to 100 c.c. with water. Add 5 c.c. of a saturated solution of ferric ammonium alum, and titrate with a standard solution of ammonium thiocyanate[7] until a permanent red tint appears, according to Volhard's well-known process (page 76). Shake the flask well during the titration to break up any clots of silver thiocyanate, which might enclose some of the solution to be titrated. The process works well with small amounts of arsenic; with large quantities, the bulky precipitate is inconvenient, and silver is expensive. Then use Mohr's process, page 290. Phosphates and molybdates should, of course, be absent.

§ 133. The Evaluation of Arsenious Oxide.

The amount of arsenic in commercial arsenious oxide can be estimated by dissolving, say, 0·5 grm. of the sample in 20 grms. of sodium hydroxide and 100 c.c. of water. Acidify the solution with hydrochloric acid, and add about 100 c.c. of a saturated solution of sodium bicarbonate. Titrate with standard iodine (a more concentrated standard solution than that indicated above may be used, say that indicated on page 312).[8]

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and the solution evaporated and dried in a weighed platinum dish. From the weight of Ag_3AsO_4 so obtained, the corresponding amount of arsenic or arsenious oxide can be readily computed.

[1] If necessary, boil to expel carbon dioxide.

[2] The precipitate formed later is soluble in nitric acid, ammonia, and ammonium nitrate solutions (J. W. Mallet and J. R. Santos, *Chem. News*, **38**. 94, 1878). Nitric acid may be liberated during the separation of silver arsenate: $Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3$. Hence the solution must be carefully neutralised. These two reagents—nitric acid and ammonia—presented a difficulty in Pearce's original method. Canby tried to eliminate the trouble with zinc oxide. As stated in the text, Bennett used a slightly acidified solution of sodium acetate in which "silver arsenate is practically insoluble."

[3] Sodium acetate facilitates the subsequent separation of silver arsenate—C. E. Avery, *Amer. J. Science* (2), **47**. 25, 1867.

[4] If the solution be alkaline, silver oxide may separate.

[5] Silver Nitrate Solution.—An ordinary nitric acid solution of silver nitrate will not do. Dissolve 17 grms. of silver nitrate crystals in 500 c.c. of distilled water. One c.c. will precipitate 0·005 grm. of arsenic, that is, 1 per cent. if 0·5 grm. of sample were originally taken. Hence, 10 c.c. is usually an excess.

[6] A white precipitate of silver chloride may remain on the filter paper undissolved. This can be neglected.

[7] Ammonium Thiocyanate Solution.—Dissolve 7·617 grms. of ammonium thiocyanate in a litre of water. Standardise the solution by titration against known weights of silver nitrate (0·8 grm. per 100 c.c. acidified with nitric acid), and 5 c.c. of a saturated solution of iron alum as indicator.

[8] If copper is present, add 2–3 grms. sodium potassium tartrate after the sodium bicarbonate, to prevent precipitation of the copper during the titration—S. Avery and H. T. Beans, *Journ. Amer. Chem. Soc.*, **23**. 485, 1901.

A mixture of arsenic and arsenious oxides may be treated in a similar manner. The titration gives the amount of arsenious oxide. A separate portion is dissolved in a similar manner, and the arsenic oxide (As_2O_5) is reduced[1] by boiling with an excess of hydrochloric acid and potassium iodide. Boil the solution until all the free iodine has been driven off, and titrate the solution by Mohr's process. This gives the total arsenious oxide. The difference between the amount obtained in the two titrations is expressed in terms of As_2O_5 by multiplying the difference by 1·1616.

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[1] For reduction by potassium iodide, see L. Rosenthaler, *Zeit. anal. Chem.*, **45.** 319, 1906; for reduction with hydriodic acid, F. A. Gooch and P. E. Browning, *Amer. J. Science* (3), **39.** 188, 1890; (3), **40.** 66, 1890; for reduction with sulphur dioxide L. R. W. McCay, *Amer. Chem. Journ.*, **7.** 373, 1885.

CHAPTER XXII.

THE DETERMINATION OF ANTIMONY.

§ 134. Antimony Sulphide.

ANTIMONY sulphide is fairly soluble in hydrochloric acid[1] containing over 20 per cent. HCl, as indicated on page 275. Hence, it is necessary to work with dilute solutions if all the antimony is to be separated as sulphide. If the solution be too dilute, antimony oxychloride will separate. It is therefore best to work with a solution acid enough, say 20 per cent. HCl, in order to prevent the precipitation of the oxychloride. The acid solution is saturated with hydrogen sulphide, diluted with, say, an equal volume of water, and again saturated with the gas,[2] as indicated on page 276.

At low temperatures, and particularly with rapid streams of hydrogen sulphide, Sb_2S_5 is precipitated.[3] The higher the temperature, and the slower the stream of gas, the greater the amount of Sb_2S_3 mixed with the Sb_2S_5.[4] In general work, therefore, we may assume that the precipitate will be a mixture of the two sulphides along with free sulphur.

The Ignition of Antimony Sulphide.—When the antimony is to be weighed as trisulphide, the excess of sulphur is removed from the precipitate by washing with, say, carbon disulphide, and the precipitate is thoroughly dried in a neutral atmosphere, say, carbon dioxide. In illustration, a precipitate of trisulphide, after drying 4 hours at 110°, weighed 0·5861 grm.; after washing with carbon disulphide and alcohol, and drying at 150° for two hours, 0·5552 grm.; again washing with carbon disulphide, and drying one hour at 180°, 0·5547 grm. Further drying an hour at

Temperature . .	200°	220°	250°	280°	300°
Weight . . .	0·5540	0·5538	0·5526	0·5523	0·5516 grm.

when the weight remained practically constant.

Influence of Oxalic Acid.—The addition of oxalic acid to a solution of antimony or tin, feebly acid with hydrochloric acid, produces a white precipitate of antimony or tin oxalate; if the solution be alkaline, fairly soluble double oxalates are formed, and the solution will remain clear without turbidity, provided sufficient alkali be present. Hydrogen sulphide produces an orange-coloured precipitate of antimony trisulphide in solutions of an antimony salt; and in solutions of a stannous salt, a black precipitate of stannous sulphide.[1] In the presence of oxalic acid, antimonic sulphide is precipitated while stannic salts are imperfectly precipitated by hydrogen sulphide. If the solution be hot, and a sufficient excess of oxalic acid be present, the stannic sulphide is not precipitated at all.

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[1] J. Lang, *Ber.*, **18.** 2714, 1885 ; J. Theile, *Liebig's Ann.*, **263.** 361, 1891 ; *Zeit. anal. Chem.*, **30.** 473, 1891 ; T. Wilm, *ib.*, **30.** 428, 1891 ; B. Brauner and F. Tomiczek, *ib.*, *Monats. Chem.*, **8.** 607, 1887 ; O. Bošek, *Chem. News*, **71.** 195, 1895 ; B. Brauner, *ib.*, **71.** 196, 1895 ; M. Berthelot, *Compt. Rend.*, **102.** 22, 84, 86, 1886 ; A. Ditte, *ib.*, **102.** 168, 212, 1886 ; G. C. Wittstein, *Vierteljahr. prakt. Pharm.*, **18.** 531, 1869.

[2] If the solution be too acid, the clear filtrate will become turbid as soon as it comes in contact with water—say a moist beaker. In that case the solution must be diluted with water, and refiltered.

[3] When the amount of hydrochloric acid in solution exceeds 10 per cent., the greater the amount of hydrochloric acid, the greater the proportion of Sb_2S_5 precipitated.

[4] Dark brown Sb_2S_5 is precipitated from cold solutions of antimonic salts, but not from antimonious salts, by an excess of hydrogen sulphide in aqueous solution.

Influence of Tartaric Acid.—When this reaction is employed for the separation of antimony and tin, it is necessary to oxidise the stannous salts to stannic. This is conveniently done by means of hydrogen peroxide. Tin, however, may be carried down with the antimony sulphide. Hence, the precipitate must be dissolved in sodium sulphide, more oxalic acid added, and the antimony sulphide again precipitated. *The addition of an excess of tartaric acid prevents the precipitation of tin along with antimony sulphide*, and renders a second precipitation unnecessary. This is the principle upon which Clarke and Henz's process[2] for the separation of tin and antimony is founded. The presence of tartaric acid also retards the separation of chloride—possibly $SbOCl$ or $SbSCl$—with the precipitate. The chloride, if present, volatilises when the precipitate is heated to 300° in a stream of carbon dioxide, and thus leads to low results.[3] The greater the amount of tartaric acid in the solution, the less the danger of loss from this cause. Thus, with the precipitate from a gram of antimony the loss on ignition was as follows:

Tartaric acid used	0	2·5	5·5	grms.
Precipitate lost on ignition	0·37	0·18	0·05	per cent.

§ 135. The Gravimetric Separation of Antimony and Tin—Clarke and Henz's Process.

Preparation of the Solution for the Precipitation.—Dissolve, say, the mixed sulphides containing less than the equivalent of 0·3 grm. of the mixed metals in a solution of sodium or potassium sulphide (page 277) in a 500-c.c. beaker. Add 6 grms. of the purest potassium hydroxide;[4] 3 grms. of tartaric acid;[5] and as much hydrogen peroxide (30 per cent.) as is necessary to decolorise the solution. Then add a volume of hydrogen peroxide equal to that already added. Boil the solution for a few minutes until the evolution of oxygen is over, and the thio-salt is oxidised.[1] Cool. Cover the beaker with a clock-glass; add 15 grms. of pure oxalic acid.[2] Carbon dioxide comes off vigorously. Boil the solution briskly for 10 minutes to decompose the hydrogen peroxide completely. The solution, now occupying about 80 or 100 c.c., is allowed to cool.

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[1] Stannous sulphide is black; stannic sulphide yellow; a mixture of the two, maroon colour. C. F. Barfoed, *Zeit. anal. Chem.*, **7.** 260, 1868; T. Scheerer, *Journ. prakt. Chem.* (2), **3.** 472, 1871; A. Carnot, *Compt. Rend.*, **103.** 258, 1886.

[2] F. W. Clarke, *Amer. J. Science* (2), **49.** 48, 1870; *Chem. News*, **21.** 124, 1870; *Zeit. anal. Chem.* **9.** 487, 1870; **21.** 114, 1882; A. Rössing, *ib*, **41.** 1, 1902; G. Vortmann and A. Metzl. *ib.*, **44.** 525, 1905; E. Lesser, *ib.*, **27.** 218, 1888; J. A. Müller, *ib.*, **34.** 171, 1895; A. Czerwek, *ib.*, **45.** 505, 1906; F. Henz, *Zeit. anorg. Chem.*, **37.** 1, 1894; A. Fischer, *ib.*, **42.** 372, 1903; A Gutbier and C. Brunner, *Zeit. angew. Chem.*, **17.** 1137, 1904; C. Ratner, *Chem. Ztg.*, **26.** 873, 1902; J. Clark, *Journ. Soc. Chem. Ind.*, **15.** 255, 1896; R. Bunsen, *Liebig's Ann.*, **192.** 317, 1878; *Zeit. anal. Chem.*, **18.** 264, 1879; A. Carnot, *Compt. Rend.*, **103.** 258, 1886; *Chem. News*, **54.** 89, 1886; H. N. Warren, *ib.*, **62.** 216, 1890; G. C. Wittstein and A. B. Clark, *Vierteljahr. prakt. Pharm.*, **19.** 551, 1870; F. P. Dewey, *Amer. Chem. Journ.*, **1.** 244, 1879; *Chem. News*, **40.** 257, 1879; O. Klenker, *Journ. prakt. Chem.* (2), **59.** 353, 1899; T. Brown. *Journ. Amer. Chem. Soc.*, **21.** 780, 1899; *Chem. News*, **81.** 178, 184, 1900; C. Hallmann, *Vergleichende Untersuchung über Methoden der quantitativen Antimon bestimmung*, Aachen, 1911; A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911.

[3] H. Rose, *Pogg. Ann.*, **98.** 455, 1856; O. Petriciolli and M. Reuter, *Zeit. angew. Chem.*, **14.** 1179, 1901; L. A. Youtz, *Journ. Amer. Chem. Soc.*, **30.** 975, 1908.

[4] That is, one-third the sum of the weights of the mixed tartaric and oxalic acids. Use potassium hydroxide "pure by alcohol."

[5] That is, 10 times the maximum weight of the mixed metals—tin and antimony—in the solution.

Precipitation of Antimony Sulphide.—Pass a rapid current of hydrogen sulphide through the cold solution and then heat it to the boiling point, all the time maintaining the current of hydrogen sulphide. Keep the flask or beaker in a boiling water bath.[3] In about 15 minutes dilute the solution to about 250 c.c. Continue the current of gas another 15 minutes. Remove the source of heat, and continue the current of gas another 10 minutes longer. Let the precipitate settle until the solution is cold.

Washing the Precipitate.—Decant the dense precipitate of antimony sulphide through a Gooch's crucible[4] which has been heated to about 300° in a stream of carbon dioxide for about an hour before cooling in the desiccator and weighing. Wash the precipitate twice by decantation with a 1 per cent. solution of oxalic acid, and twice by decantation with very dilute acetic acid. Both washing liquids should be boiling and kept saturated with hydrogen sulphide.[5] The filtering and washing should be done as quickly as possible, since the antimony sulphide is liable to decompose or deflocculate and pass into solution.[6] The precipitate will be contaminated with some sulphur. It is best to remove[7] most of the sulphur by washing three times with alcohol, then with a mixture of equal parts of alcohol and carbon disulphide, then with alcohol, and finally with ether.

The Ignition of the Precipitate.—Dry the precipitate and heat it gradually to between 250° and 300° in a stream of carbon dioxide for between 30 and 60 minutes. The heating is conveniently done in Paul's drying oven,[8] fig. 127. The sulphur in the precipitate is volatilised, and the antimony pentasulphide is transformed into the grey trisulphide. The sulphur will all have volatilised in about an hour.[9] The crucible is cooled and weighed. When two successive weighings do not differ by more than 0·0005 grm., the operation is complete. The weight of the precipitate—Sb_2S_3—multiplied by 0·8568 represents the corresponding amount of Sb_2O_3.

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[1] All the peroxide cannot be decomposed at this stage.

[2] That is, 50 times the weight of the mixed metals in the solution. The hot solution should be saturated with oxalic acid.

[3] If the solution be kept cold, the antimony sulphide will be difficult to filter so as to form a clear solution; if the gas be passed at once into the boiling solution, the precipitate is liable to stick tenaciously to the sides of the beaker; and if the gas be passed into the cold solution and the solution gradually heated to boiling during the passage of the gas, the precipitate is granular, and washes easily—S. P. Sharples, *Amer. J. Science* (2), **50**. 248, 1870; *Chem. News*, **22**. 259, 1870.

[4] If arsenic be present, it too will be precipitated as sulphide. Filter tubes, figs. 53 *B* and *C*, can be used. W. Gibbs and E. R. Taylor, *Amer. J. Science* (2), **44**. 215, 1867; R. Fresenius, *Zeit. anal. Chem.*, 8. 155, 1869.

[5] At this stage the antimony can usually be determined volumetrically, with a great saving in time, if a standard solution is ready.

[6] C. Friedheim and P. Michaelis, *Zeit. anal. Chem.*, **34**. 505, 1895; J. Theile, *ib.*, **30**. 479, 1891. The treatment described in the text is better than washing with carbon disulphide alone, since the latter may be entangled with the precipitate, and not pass through the filter paper. Antimonic sulphide—Sb_2S_5—is not decomposed into antimonious sulphide—Sb_2S_3—and sulphur by the treatment with carbon disulphide. For an extraction apparatus, see fig. 134, page 343.

[7] See page 343 for a discussion on removing sulphur from sulphides.

[8] T. Paul, *Zeit. anal. Chem.*, **31**. 537, 1892. In fig. 127, *T* represents the thermometer, *B* a Habermann's wash-bottle containing sulphuric acid for cleaning the carbon dioxide. The carbon dioxide must be free from air, or some of the antimony will be oxidised to Sb_2O_4. F. Henz's gas generator (*Chem. Ztg.*, **26**. 386, 1902) is one of the best "CO_2 generators" for this experiment.

[9] The heating should not extend much more than an hour, or some antimony sulphide may be lost by volatilisation. See L. A. Youtz, *Journ. Amer. Chem. Soc.*, **30**. 975, 1908.

EXAMPLE.—The sulphide from 1 grm. of material, after half an hour's ignition in Paul's oven, as indicated above, gave, on first weighing, 0·02423 grm. Sb_2S_3. After ignition for another 15 minutes, the sulphide weighed 0·02418 grm. Hence, 0·0242 × 0·8568 = 0·0207 grm., that is, 2·07 per cent of Sb_2O_3.

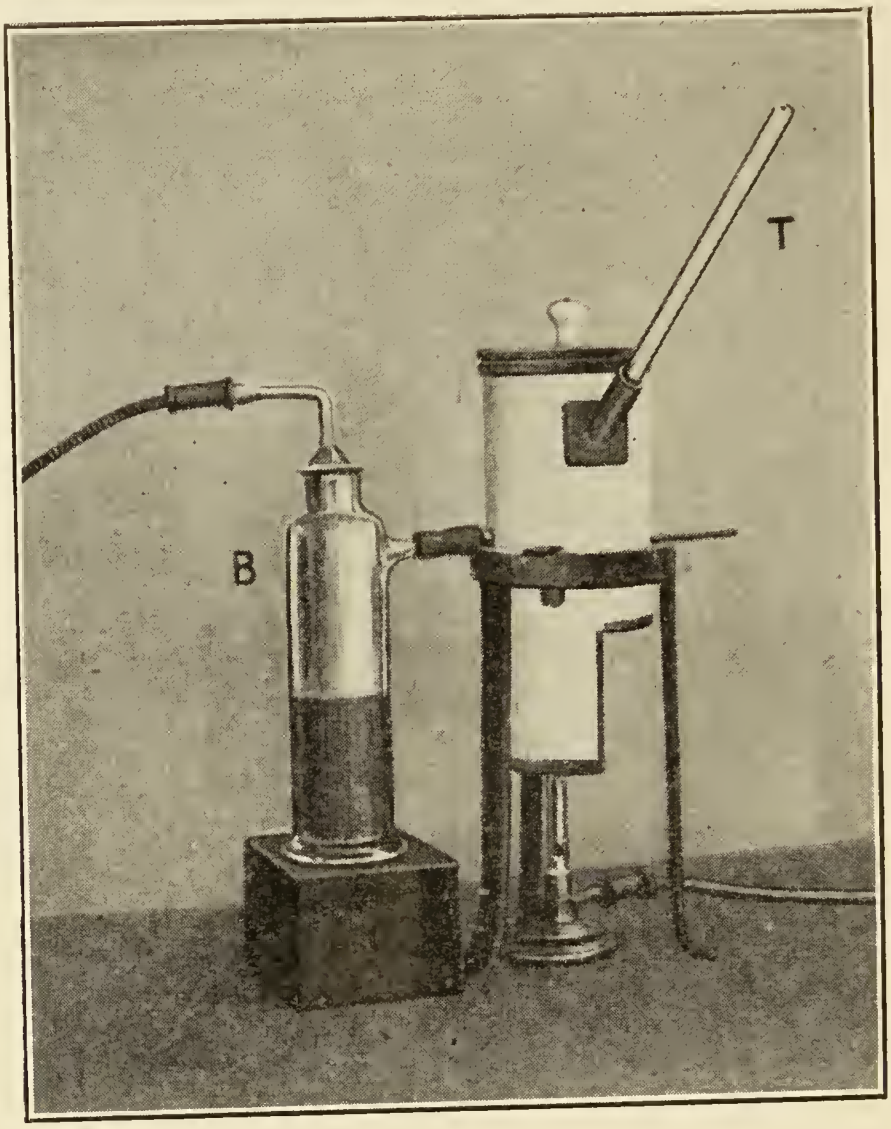

FIG. 127.—Ignition of antimony sulphide.

The Accuracy of the Process.—One objection to this process is the great amount of oxalic and tartaric acid required to keep the tin in solution.[1] The chief errors arise from (1) the presence of free mineral acids; (2) the use of too concentrated solutions; and (3) error in assuming the ignited precipitate is normal trisulphide, Sb_2S_3. In illustration of the kind of separations which can be obtained with this method, the following numbers are cited for mixtures of known amounts of antimony and tin :—

Table XLVII.—Test Analyses of Mixtures of Antimony and Tin.

Antimony.		Tin.	
Used.	Found.	Used.	Found.
0·0463	0 0462	0·2555	0·2532
0·0463	0·0461	0·1017	0·1011
0·0924	0·0923	0·0103	0·0113
0·1855	0·1853	0·1017	0·0999

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[1] W. Dancer (*Journ. Soc. Chem. Ind.*, **16.** 403, 1897) and J. Marburg (*Zeit. anal. Chem.*, **39.** 47, 1900) first precipitate the tin with an excess of lime water.

If the antimony is to be separated from a complex enamel, the values for the antimony will not, of course, be so concordant as this. The tin was here determined by the electrolytic process, page 312. The method thus gives good results, although it is somewhat laborious. Consequently, volumetric processes are employed wherever practicable. The volumetric process, however, is not satisfactory when less than 1 per cent. of antimony is present. For many purposes the "iron precipitation" of antimony is the most convenient process for the separation of antimony from tin.[1]

Effect of Molybdenum.—The separation of arsenic and tin is even sharper than the separation of antimony and tin by Clarke's process. To separate molybdenum from "stannic" tin requires a modification of the process. Antimony and molybdenum are precipitated together.[2] "By adding an alkaline sulphide in excess to a solution containing a molybdate," says Clarke, "and then decomposing the thio-salt with a considerable quantity of dilute hydrochloric acid, and allowing the whole to stand overnight in a warm place, the molybdenum is precipitated. The sulphide thus obtained can be easily washed with a mixture of dilute hydrochloric acid and ammonium chloride. If now, by this process, we throw down tin and molybdenum together, every trace of the former metal may be dissolved out by boiling the mixed sulphides for about three-quarters of an hour with oxalic acid (20 grms. of oxalic acid per gram of tin). It is best to have present in the solution, while boiling, a little dilute hydrochloric acid. If antimony be present, it is necessary, just before ceasing to boil, to add to the solution an equal volume of a saturated solution of hydrogen sulphide to reprecipitate any antimony which may have gone into solution."[3]

§ 136. Weller's Volumetric Iodide Process for Antimony.

The solution containing the antimony and tin may be divided into two parts: the antimony determined in one part by Weller's or by Györy's process, and the tin in the other part by one of the processes indicated on page 310 *et seq.* In Weller's process[4] the antimony is all oxidised to antimony pentachloride; mixed with potassium iodide; and the amount of iodine liberated by the reduction of the antimonic to antimonious chloride determined by titration with sodium thiosulphate, as indicated on page 352, or by stannous chloride—the alternative process here described. Which process—thiosulphate or stannous chloride—is used will often be determined by the most convenient standard solutions.

The Oxidation of Antimonious to Antimonic Chloride.—The sulphide is transferred to a 600-c.c. Erlenmeyer's flask, and dissolved by boiling with a mixture of concentrated hydrochloric acid and potassium chlorate. The latter is added in small portions at a time. The object is to convert the antimony trichloride—

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[1] For the "rapid" electro-deposition of both antimony and tin from the ammonium sulphide solution of the two sulphides; digestion of the mixed metals with aqua regia; and titration of the antimony by Weller's process, see D. J. Demorest, *Journ. Ind. Eng. Chem.*, **2**. 80, 1910; *Chem. News*, **101**. 260, 1910.

[2] For the separation of antimony and molybdenum, see page 415.

[3] Tungsten gives discordant results. Sometimes the tungsten sulphide seems to dissolve like tin; at others, the solution is only partial—F. W. Clarke (*l.c.*).

[4] A. Weller, *Liebig's Ann.*, **213**. 364, 1882; L. A. Youtz, *School Mines Quart.*, **24**. 135, 407, 1903; *Zeit. anorg. Chem.*, **37**. 337, 1903; A. Kolb and R. Formhals, *ib.*, **58**. 189, 202, 1908; E. Schmidt, *ib.*, **34**. 453, 1910; H. Causse, *Compt. Rend.*, **125**. 1100, 1897; H. Giraud, *Bull. Soc. Chim.* (2), **46**. 504, 1886; G. Rollin, *Ann. Chim. Anal. App.*, **6**. 114, 1902; G. von Knorre, *Zeit. angew. Chem.*, **1**. 155, 1888; M. Rohmer, *Ber.*, **34**. 1565, 1901; J. Darroch, *Chem. Eng.*, **4**. 162, 1906; G. S. Jamieson, *Journ. Ind. Eng. Chem.*, **3**. 250, 1911.

$SbCl_3$—into the pentachloride—$SbCl_5$.[1] When the free chlorine and chlorine oxides have been driven off by boiling, and the volume of the solution is about 50 c.c., let the solution cool. When cold, add 20 c.c. of concentrated hydrochloric acid, and dilute the solution to about 200 c.c. with recently boiled distilled water (cold).

The Liberation of Iodine.—Add, say, 3 grms. of potassium iodide dissolved in 10 c.c. of water. Stir the solution thoroughly. The antimony pentachloride is reduced to the trichloride. The reaction is represented:

$$SbCl_5 + 2KI \rightleftharpoons SbCl_3 + 2KCl + I_2.$$

The solution now has a brown colour due to the liberated iodine. The strong acidity of the solution prevents the precipitation of antimony oxychloride. Dilute the solution to about 400 c.c.

Titration with Stannous Chloride.—Titrate the solution, at once,[2] with a standard solution of sodium thiosulphate or of stannous chloride.[3] The solution should be well shaken during the titration, particularly towards the end. When the end point is near, the solution becomes pale yellow. Then add a couple of drops of starch solution (page 286). Shake the solution vigorously, and titrate until the blue colour of the starch iodide has disappeared. The end point is very sharp, and, consequently, the standard solution must be added cautiously drop by drop. If any after-bluing occurs, it will be due to secondary reactions and may be ignored. The reaction which takes place during the titration may be represented:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI.$$

Influence of Foreign Metals.—Arsenic reacts in a similar manner to antimony, and cupric salts also liberate iodine from potassium iodide.[4] Bismuth iodide resembles the colour of free iodine in solution and consequently obscures the end point, but does not otherwise interfere. Tin, as stannic chloride, does no harm.

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[1] Any stannous salts which may be present are also oxidised to stannic salts.

[2] Iodine titrations are usually made in Erlenmeyer's flasks, not in beakers, on account of the volatility of the iodine during the titration. A large excess of potassium iodide lessens the danger of losing iodine in this way. For a similar reason, iodine titrations should be performed immediately the iodine has separated; and the solution should be cold. J. Wagner (*Zeit. anal. Chem.*, **27.** 137, 1888; C. R. A. Wright, *Chem. News*, **21.** 163, 1870) found that with the same amount of solution of sodium thiosulphate:

Temperature	16°	30°	38°	50°	75°	83°	91°
Iodine sol.	39·6	39·8	40·0	40·1	40·7	40·9	41·4 c.c.

These numbers show that the higher the temperature, the less the amount of thiosulphate required in titrating a given amount of iodine; and conversely. E. Sherer, *Chem. News*, **21.** 141, 1870.

[3] STANDARD STANNOUS CHLORIDE.—Dissolve, say, 10 grms. of stannous chloride in 60 grms. of hydrochloric acid (sp. gr. 1·12). Dilute the solution to a litre. Dissolve 0·2 grm. of metallic antimony in concentrated hydrochloric acid and potassium chlorate (or bromine) in the cold. Metallic antimony is but slowly attacked by hot hydrochloric acid and potassium chlorate. Boil the solution to get rid of the chlorine oxides (or bromine). Cool. Add potassium iodide as indicated in the text. The titration is made as indicated in the text. The antimony equivalent of the standard solution of stannous chloride is thus simple arithmetic. Weller titrates with standard sodium thiosulphate, but I prefer the stannous chloride, if the preparation of the solution is not inconvenient. The objection to the stannous chloride titration is the instability of the solution due to oxidation. The objection to the thiosulphate titration rests on the known reaction between sodium thiosulphate and strong acids. For the sodium thiosulphate titration, see page 352.

[4] Arsenic can be removed by boiling the solution with concentrated hydrochloric acid; copper and bismuth can be removed by washing the precipitated sulphides on a filter paper with sodium sulphide.

Influence of Hydrochloric Acid.—Too much hydrochloric acid gives high results owing to the action of the acid on the potassium iodide. The solution should not contain much more than about one-fifth of its volume of concentrated hydrochloric acid (sp. gr. 1·16). Too little hydrochloric acid leads to the separation of basic chlorides or iodides of antimony. By following the above directions—boiling down to 50 c.c.—an acid of constant strength is obtained—approximately 20 per cent. HCl—and diluting the solution as indicated, satisfactory results will be obtained. If the acidity of the solution used for standardising the stannous chloride be the same as that of the sample under investigation, and the general treatment be the same,[1] determinations can be made more quickly and as accurately as the gravimetric process when over 1 per cent. of antimony is present. If less than 1 per cent. be present, use the gravimetric process of Clarke.

Relation of Weller's to Mohr's Process.—Mohr's process for arsenic (page 290) is quite satisfactory when applied to antimony; and Weller's process for antimony is quite satisfactory when applied to arsenic.[2] A comparison of the two processes is interesting. The same general equation applies to both:

$$R_2O_3 + 2I_2 + 2H_2O \rightleftharpoons R_2O_5 + 4HI$$
$$\text{Mohr} \rightarrow \qquad \leftarrow \text{Weller}$$

In Mohr's process, the reverse action indicated in the equation is prevented by keeping down the concentration of the hydriodic acid by means of an excess of alkali (sodium bicarbonate) in the solution. In Weller's process, the reverse action is prevented by the relatively strong acidity of the solution.

Comparison Determinations.—To illustrate the results obtained in a separation of antimony and tin, the following duplicate determinations of the percentage amount of antimony with each of the processes here recommended, might be quoted:—

Henz and Clarke's process.	Weller's process.	Györy's process.
26·96	26·33	26·52
26·10	26·23	26·59

§ 137. Györy's Volumetric Bromate Process for Antimony.

This process[3] may be employed as an alternative to that which precedes. Chemists who use this process regularly are enthusiastic about its merits. The sample under investigation is dissolved in a 250-c.c. Erlenmeyer's flask with 20 c.c. of concentrated hydrochloric acid and a little potassium chlorate or a few drops of bromine. Boil the solution.

Reduction of the Antimonic and Arsenic Salts.—Add, say, 0·75 grm. of crystalline sodium sulphite in order to reduce the antimonic to the antimonious chloride, and the arsenic to arsenious chloride.[4] Boil vigorously until the solution is reduced to about half its former volume. This drives off the sulphur dioxide,[1] and volatilises the arsenic. Rinse the sides of the flask with hot water, and add 10 c.c. of hydrochloric acid to the solution.

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[1] Some prefer to make a blank test and find the amount of stannous chloride or sodium thiosulphate needed when no antimony is present. For the influence of organic substances on iodine titrations, see J. Klaudie, *Listy Chemické*, **12.** 91, 1888. Fatty acids and sugar have no action; aldehyde, phenol, tannin, and the aromatic alcohols give high results.

[2] T. Smith, *Journ. Amer. Chem. Soc.*, **21.** 769, 1899; F. A. Gooch and P. E. Browning, *Amer. J. Science* (3), **40.** 66, 1891.

[3] S. Györy, *Zeit. anal. Chem.*, **32.** 415, 1893; H. Nissenson and P. Siedler, *Chem. Ztg.*, **27.** 749, 1903; E. Schmidt, *ib.*, **34.** 453, 1910; J. B. Duncan, *Chem. News*, **95.** 49, 1907; H. W. Rowell, *Journ. Soc. Chem. Ind.*, **25.** 1181, 1906; F. Foerster, *Zeit. Elektrochem.*, **15.** 232, 1909; A. Christensen, *Pharm. Ztg.*, **41.** 326, 1896.

[4] The stannic chloride is not reduced.

The Titration.—Heat the solution to about 80° or 90°, and titrate with a standard solution of potassium bromate[2] until nearly all the antimony is oxidised to antimonic chloride.[3] Add 3 drops of methyl orange, and continue the titration until the tint of the methyl orange is destroyed.[4] The solution should be thoroughly agitated during the titration, so that local excesses of bromate are not formed.[5] If very little bromate be needed, the indicator may be added before the titration. This, however, is an extreme case. If over 10 c.c. of bromate are needed, it is best to run in the greater part of the bromate before adding the indicator. The indicator has a tendency to fade, and if it be used from the start on an "unknown," it is necessary to add more from time to time as the titration progresses. The first titration may be used for finding the approximate amount of bromate needed. The solution is not run from the burette much faster than 30 c.c. per minute. The reaction is represented by the equation:

$$KBrO_3 + HCl + 3SbCl_3 = KCl + HBr + 3Sb + 3H_2O.$$

Any further addition of bromate destroys the colour of the methyl orange, probably owing to the liberation of bromine by the action of free acid on the bromate, for if bromate be added after the methyl orange has lost its colour, the yellow colour of the bromine appears in a short time.

Influence of Foreign Substances.—The process works well in the presence of lead, zinc, tin, silver, chromium, and sulphuric acid, since these substances have no appreciable effect on the result. The presence of large amounts of calcium, magnesium, and ammonium salts furnishes high results. Iron and copper are partly reduced by the sodium sulphite in the solution, and hence react with the bromate, giving high results. Rodwell states that 1 per cent. of iron raises the amount of antimony by 0·02 per cent., but 5 per cent. of iron raises the amount of antimony but little more. Rodwell also states that, for every 0·1 per cent. of copper in the sample up to 1 per cent., 0·012 per cent. of antimony should be subtracted.[6]

Accuracy of the Process.—The most important sources of error are: (1) incomplete expulsion of sulphur dioxide; (2) the imperfect volatilisation of arsenic, if present; and (3) over-titration, when too little hydrochloric acid is present, owing to the slowness of the reaction. In illustration of the accuracy of the process, the following determinations, by Rowell, may be quoted:—

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[1] The amount of antimony "lost" by volatilisation or reoxidation is inappreciable. Most of the arsenic will be volatilised, since arsenious chloride is fairly volatile from boiling solutions. See page 271.

[2] POTASSIUM BROMATE SOLUTION.—Dissolve, say, 2·7852 grms. of the pure salt in a litre of water. To standardise the solution, dissolve 0·2 grm. of metallic antimony in hydrochloric acid and potassium chlorate as indicated, page 300. The reduction and titration of the resulting solution are conducted as indicated in the text.

[3] If lead be present, and the lead chloride separates as the solution cools, boil the solution again in order to keep the lead chloride in solution while the titration is in progress.

[4] Some prefer to use, as indicator, a solution of indigo made by dissolving powdered indigo in fuming sulphuric acid. Neutralise the solution with calcium carbonate; dilute with 10 times its volume of water; and filter the blue liquid. Add 3 drops of this solution at the start, and more when the reaction is nearly completed. The blue passes through various shades of greenish yellow into pale green. The colour is discharged with a drop of bromate in excess. The indigo solution is not so sensitive an indicator as the methyl orange, and the results with the indigo are a little higher than with methyl orange.

[5] Otherwise the results will be high owing to the loss of bromate before it attacks the antimony.

[6] For the reduction of the bromate by stannous salts, see F. Fichter and E. Müller, *Chem. Ztg.*, **37**. 309, 1913.

Table XLVIII.—Test Analyses of Antimony Ores.

Nature of mixture.	Antimony (per cent.).	
	Volumetric bromate process.	Gravimetric (as Sb_2S_3).
Antimony sulphide	71·40	71·35
Stibnite (As, Fe)	71·20	71·35
Lead : antimony	9·42	9·37
Lead : arsenic : antimony	8·65	8·70
Lead : antimony : tin	2·13	2·20

The analysis can thus be conducted with an accuracy approaching 0·1 per cent. in samples containing 10 per cent. of antimony. It may be a little difficult at first to get concordant results, but once the manipulation is mastered, the process gives little trouble. J. B. Duncan informs me that "duplicates on a straight assay running 99·6 per cent. metallic antimony should agree exactly."

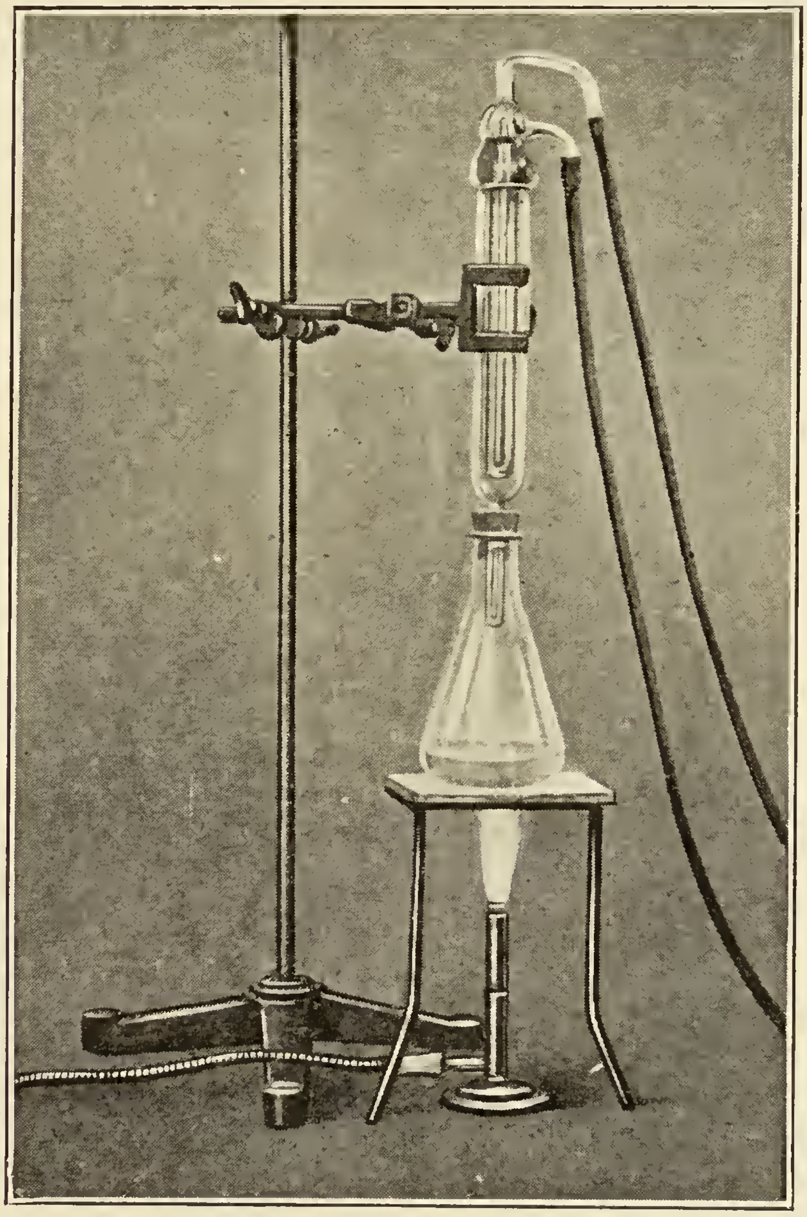

FIG. 128.—Reflux condenser (see page 582).

The Influence of Arsenic.—The process indicated above can be employed for the determination of arsenic, but the boiling of the solution in open vessels to expel the sulphur dioxide will not do. The boiling must be conducted in a flask fitted with a reflux condenser (fig. 128). If the antimony is to be determined, and arsenic is present in the sample, the latter must be removed, as indicated above, by boiling the solution down to half its volume in presence of sodium sulphite. If more than 2 or 3 per cent. of arsenic be present, add 20 c.c. more concentrated hydrochloric acid, and 5 c.c. of a saturated aqueous solution of sulphur dioxide. Boil the liquid down again. There is no danger of an appreciable loss of antimony if the temperature be kept below 120°. An artificial mixture of antimony and arsenic so treated furnished 91·09 per cent. of antimony, when 90·91 per cent. was actually present.

§ 138. The Volumetric Determination of Antimony and Arsenic in presence of Tin.

The arsenic and antimony in a solution containing antimony, arsenic, and tin can be separately determined by the bromate process. The mixture is dissolved and oxidised as indicated for Györy's process. Make the solution up to, say, 200 c.c. Boil off the arsenic in an aliquot portion, say, 100 c.c., as indicated above, and titrate the solution for antimony with potassium bromate. The arsenic and antimony can be determined together in the other aliquot portion by proceeding as indicated above, but boiling down the solution in a reflux condenser (fig. 128). The difference in the two titrations represents the potassium bromate which is equivalent to the arsenic.[1]

Example.—A solution was made up to 200 c.c. as indicated above. The antimony in 100 c.c. required 24·7 c.c. of the potassium bromate solution. This corresponds with $24·7 \times 0·0006432 = 0·0159$ grm. of Sb_2O_3 in half the sample. The other portion, boiled with a reflux condenser, required 52·1 c.c. of the bromate solution. Hence, $52·1 - 24·7 = 27·4$ c.c. of the bromate were required for the arsenic titration $27·4 \times 0·0004417 = 0·0121$ grm. of As_2O_3 in half the sample.

§ 139. Metallic Precipitation.

In the ordinary zinc : carbon cell, if the metallic zinc be replaced successively by manganese, aluminium, and magnesium, the voltage of the cell is increased; and conversely, if the zinc be similarly replaced by cadmium, iron, and cobalt, the voltage is diminished. The order in which the metals can be thus arranged is the same as the order in which the metals displace one another in their salts. The order is approximately :

K, Na, Mg, Al, Mn, Zn, Cd, Fe, Co, Ni, Sn, Pb, Sb, Bi, As, Cu, Hg, Ag, Pt, Au,

and the series is called the electrochemical series of the metals. The order varies a little with different solutions. A metal on the left in the series will generally displace another metal on the right from its salt solution. Secondary reactions may prevent the actual precipitation of the metal. In many cases the displacement is so complete that the reaction can be used in quantitative analysis. What metals are precipitated often depends upon the acidity of the solution as well as on the metal used as precipitating agent. In illustration of the more important metals used as precipitating agents, magnesium precipitates zinc, cadmium, thallium, iron, cobalt, nickel, tin, lead,[2] antimony,[3] bismuth, copper,[1] mercury, silver,[2] platinum, and gold. Some part of the antimony may be evolved as a gas when solutions containing antimony are treated with magnesium or zinc; and arsenic is also lost in this way when its solutions are treated with zinc, magnesium, and iron.[3] Aluminium precipitates lead,[4] antimony,[5] tin, copper, and silver,[6] etc. Zinc precipitates cadmium, cobalt,[7] nickel,[7] tin, lead,[8] antimony, bismuth, arsenic, copper,[9] mercury, platinum, gold, etc.; but not iron.[10] Cadmium precipitates copper, lead, silver,[11] antimony, tin, etc. Iron precipitates bismuth,[12] antimony,[13] copper, mercury, silver, lead, gold, etc. In the presence of stannic chloride, arsenic is also precipitated. Metallic iron also reduces ferric to ferrous salts, stannic to stannous salts, etc. Tin precipitates antimony, arsenic, copper, mercury, silver, gold, etc. Copper precipitates mercury, silver, gold, etc., but not tin; lead precipitates bismuth,[14] etc.

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[1] Rather more hydrochloric acid is required in the case of antimony than arsenic in order to prevent the precipitation of antimony during the titration, as a result of the increasing dilution of the solution.

[2] W. Schulte, *Metallurgie*, **6**. 214, 1909.

[3] S. Kern, *Chem. News*, **32**. 309, 1875; E. G. Bryant, *ib.*, **79**. 75, 1899.

Precipitation of Antimony in the Presence of Tin—Tookey's Process.—The separation of antimony from tin by precipitation of the antimony, as metal, from a hot hydrochloric acid solution by means of metallic iron[15] was proposed by Tookey in 1862.[16] The process can be conducted in the following manner:—Dissolve the mixed sulphides in a warm mixture of hydrochloric acid and potassium chlorate, and boil off the chlorine. The solution should contain about 12 per cent., and not less than 2 per cent. of hydrochloric acid, or some tin may be precipitated. Place some coarse granules of pure[17] metallic iron in the solution very nearly at the boiling temperature. Add more hydrochloric acid as the iron dissolves. When all the antimony is precipitated,[1] filter the solution as quickly as possible, since some antimony may redissolve when the solution is exposed to the air. An excess of iron is necessary, and the precipitated antimony must be mixed with the iron during the filtration.[2] The mixture of metallic antimony and iron can then be dissolved in a mixture of hydrochloric acid and potassium chlorate, and the antimony determined by precipitation as sulphide, etc.

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[1] A. Villiers and F. Borg, *Bull. Soc. Chim.* (3), **9**. 602, 1893; *Chem News*, **68**. 263, 1893.

[2] E. G. Bryant, *Chem. News*, **79**. 75, 1899.

[3] A. Roussin, *Journ. Pharm. Chim.* (4), **3**. 413, 1866; *Chem. News*, **14**. 27, 1866. W. N. Hartley, *ib.*, **14**. 73, 1866 (failed to precipitate iron with magnesium); S. Kern, *ib.*, **33**. 236, 1876; T. L. Phipson, *ib.*, **9**. 219, 1864; A. Commaille, *Compt. Rend.*, **63**. 556, 1866; F. Clowes and R. M. Caven, *Chem. News*, **76**. 297, 1897; E. G. Bryant, *ib.*, **79**. 75, 1899. J. G. Hicks and E. F. Smith (*Journ. Amer. Chem. Soc.*, **16**. 822, 1894) have studied the action of magnesium on manganous salts.

[4] A. H. Low, *Journ. Anal. App. Chem*, **4**. 12, 1891; **6**. 664, 1892; J. E. Williams, *Eng. Min. Journ.*, **53**. 641, 1892.

[5] W. Schulte, *Metallurgie*, **6**. 214, 1909.

[6] N. Tarugi, *Gaz. Chim. Ital.*, **33**. ii. 223, 1903.

[7] J. L. Davies, *Journ. Chem. Soc.*, **28**. 311, 1875.

[8] F. Stolba (*Journ. prakt. Chem.* (1), **101**. 150, 1867; *Chem. News*, **17**. 2, 1868) precipitates lead from lead salts quantitatively by metallic zinc in the presence of hydrochloric acid on a water bath. L. T. Merrill, *Eng. Min. Journ.*, **91**. 56, 1911; A. Eckenroth, *Pharm. Ztg.*, **40**. 528, 1895; F. Mohr, *Zeit. anal. Chem.*, **12**. 142, 1873; C. Rössler, *ib.*, **24**. 1, 1885.

[9] J. C. Shengel and E. F. Smith, *Journ. Amer. Chem. Soc.*, **21**. 932, 1899; *Chem. News*, **81**. 134, 1900.

[10] M. Demarçay, *Bull. Soc. Chim.* (2), **32**. 610, 1879.

[11] A. W. Clasen, *Journ. prakt. Chem.* (1), **97**. 217, 1866; *Chem. News*, **13**. 232, 1866.

[12] J. Clark (*Journ. Soc. Chem. Ind.*, **19**. 26, 1900) for the separation of bismuth and lead. J. G. Gallety and G. C. Henderson (*Analysis*, **34**. 389, 1909) recommend the process using a hot solution containing $2\frac{1}{2}$ per cent. of free nitric acid

[13] A. Thiel and K. Keller, *Zeit. anorg. Chem.*, **68**. 42, 1910.

[14] C. Ullgren, *Berzelius' Jahrb.*, **21**. 148, 1842; A. Patera, *Zeit. anal. Chem.*, **5**. 226, 1866, separate bismuth from lead in this way; but according to O. Steen (*Zeit. angew. Chem.*, **8**. 531, 1895) the error lies between 20 and 30 per cent.

[15] J. L. Gay Lussac precipitated antimony in the presence of tin by means of metallic tin in hydrochloric acid solution—J. L. Gay Lussac, *Ann. Chim. Phys* (2), **46**. 222, 1831 If zinc is used instead of iron, some antimony may be lost as hydride. No antimony is lost as hydride when iron is used—M. Dupasquier, *Compt. Rend.* **14**. 514, 1842. J. H. Mengin (*Compt. Rend.*, **119**. 224, 1894; *Chem. News*, **70**. 93, 1894) precipitates the antimony with metallic tin.

[16] C. Tookey, *Journ. Chem. Soc.*, **23**. 107, 1870; J. Attfield, *Pharm. Journ.* (2), **10**. 512, 1870; A. W. Clasen, *Journ. prakt. Chem.* (1), **92**. 477, 1864; *Chem. News*, **13**. 232, 1866; O. Low, *Vierteljahr. prakt. Chem.*, **14**. 406, 1864; A. Carnot, *Compt. Rend.*, **114**. 587, 1892; J. H. Mengin, *ib.*, **117**. 224, 1894; M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 27, 1911.

[17] C. Rammelsberg recommends iron reduced in hydrogen gas. Bright piano wire will do quite well.

Working with known mixtures of stannic chloride and antimony trichloride, Hoffmann found the following results:—

Antimony . . .	0·1	0·2	0·4	0·1	0·2	0·4	grm.
Tin used . . .	0·4343	0·4343	0·4343	0·8686	0·8686	0·8686	grm.
Tin found . . .	0·4336	0·4337	0·4338	0·8684	0·8687	0·8685	grm.
Error	−0·0007	−0·0006	−0·0005	−0·0002	+0·0001	−0·0001	grm.

The results are therefore quite satisfactory.[3]

I have had no experience with the electrolytic processes for antimony.

§ 140. The Evaluation of Antimony Compounds.

Antimony oxide may be evaluated by a method similar to that used for the arsenic compounds (page 293). Add, say, 0·1 grm. of antimonious oxide to 20 c.c. of water; heat the solution to boiling; add tartaric acid in small quantities at a time until the oxide is completely dissolved.[4] Neutralise the solution with sodium bicarbonate; and add 10 c.c. more of the sodium bicarbonate solution. Titrate with iodine using starch as indicator as described for Mohr's process for arsenic, page 290.[5] Since $Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5$, every gram of iodine represents 0·564 grm. of Sb_2O_3. Antimonic compounds are reduced as indicated under Győry's process, and estimated by Mohr's or by Győry's process.[6]

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[1] If the volume of the solution is small this will take about 20 minutes.

[2] A. W. Clasen (*l.c.*) has shown that the precipitated antimony is perceptibly soluble in hot or cold hydrochloric acid of various strengths, and hence antimony may be "lost." By following the plan described in the text, this loss is made negligibly small.

[3] The tin was determined in the filtrate, after the separation of the antimony, by precipitation as sulphide. G. Panajotow (*Ber.*, 42. 1296, 1909) separates antimony from tin by precipitating the antimony as sulphide from a solution containing 15 per cent. of HCl, at ordinary temperatures. The tin remains in solution. The results seem to be good—A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911.

[4] The tartaric acid keeps the antimony oxide in solution—F. H. Alcock, *Pharm. Journ.*, 362, 1900.

[5] Titrate at once, or antimonious hydrate may be precipitated.

[6] R. Rickmann (*Zeit. angew. Chem.*, 25. 1518, 1912) detects antimony in enamels, by cleaning the enamel free from adhering iron, and then boiling the powdered enamel with a 4 per cent. solution of acetic acid (or 2 per cent. tartaric acid). Divide the solution into two parts. Test one part with hydrogen sulphide, and titrate the other part with standard permanganate. If antimony is present, and no permanganate is consumed, it is inferred that the enamel contains a metantimoniate which Rickmann says is harmless.

CHAPTER XXIII.

THE DETERMINATION OF TIN.

§ 141. The Metallic Precipitation of Tin.

Tin may be conveniently precipitated in the metallic state by means of metallic zinc, aluminium, or cadmium. This reaction also offers a convenient method of separating tin in the filtrate from the antimony sulphide obtained in Clarke and Henz's process.[1] Boil off the hydrogen sulphide.

Precipitation of Metallic Tin.—Place a piece of zinc [2] (foil, ribbon, or stick) in the solution, and heat the solution nearly to the boiling point over a small flame. In about 20 minutes, test a few drops of the clear liquid for tin by means of "H_2S" water. If necessary, heat the solution a little longer until all the tin is precipitated. Decant the liquid through a small filter paper, and transfer the metallic tin and zinc to the filter paper. Wash with water.[3]

Conversion of the Metallic Tin into Stannic Oxide.—Rinse the metallic tin and zinc into a 250-c.c. beaker. The total volume of the liquid will be about 10 c.c. Add 10 c.c. of nitric acid, and cover the beaker with a clock-glass.[4] When all the zinc is dissolved, and the tin oxidised, dilute the solution to 40–50 c.c. Carefully heat the solution to boiling, and stir vigorously. Let settle. Add 5 grms. of ammonium nitrate; filter and wash with a 5 per cent. solution of ammonium nitrate. Burn the filter paper in a crucible. Moisten the ash with nitric acid; dry in a water bath; ignite the precipitate, gently at first, and finally over a blast. Weigh the precipitate as SnO_2.

Tin and antimony can be together precipitated by cadmium, and weighed. By digesting the mixed metals in hydrochloric acid, the tin dissolves, and antimony remains behind. The antimony can be washed, dried, and weighed. The amount of tin is obtained by difference.[5] Stannic salts are reduced to stannous salts by the metallic iron, but no tin is precipitated.

§ 142. The Precipitation of Tin as Hydroxide—Löwenthal's Process.

There are two stannic oxides corresponding with SnO_2. The one is called α-stannic acid, or α-metastannic acid; the other, β-stannic acid, or β-metastannic acid.[1] α-stannic acid dissolves quickly in cold dilute mineral acids—nitric, hydrochloric, and sulphuric acids. The solution, on prolonged boiling, deposits the β-acid, which is practically insoluble in dilute acids.[2] Salts corresponding with the two stannic acids are known.

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[1] C. Ratner, *Chem. Ztg.*, **26**. 873, 1902; G. Buchner, *ib.*, **18**. 1904, 1894; L. Vignon, *Compt. Rend.*, **107**. 734, 1888.

[2] Free from tin. For lead in place of zinc, see A. Pleischl, *Dingler's Journ.*, **164**. 200, 1862.

[3] If a stick of cadmium is used for the precipitation, the cadmium can be easily separated from the tin. The latter is washed first with water; then with alcohol; melted to a button under stearic acid in a porcelain crucible; and cleaned by washing with benzene—L. Moissenet, *Compt. Rend.*, **51**. 205, 1860.

[4] If the reaction be too violent, dilute the solution with cold water. If the action ceases, warm the solution.

[5] J. H. Mengin, *Compt. Rend.*, **119**. 224, 1894; J. L. Gay Lussac, *Ann. Chim. Phys.* (2), **46**. 222, 1831.

In Löwenthal's process[3] for the determination of tin, ammonia is added to the solution containing stannic chloride[4] until a permanent precipitate just begins to form. Add dilute hydrochloric acid, drop by drop, with constant stirring, until the precipitate is all just redissolved. Add a cold saturated solution of ammonium nitrate[5] to the solution and boil for some time.[6] When all the tin is precipitated, let the precipitate settle, and wash by decantation with a 5 per cent. solution of ammonium nitrate until the precipitate is free from chlorides.[7] After burning the filter paper, moisten the ash with nitric acid, evaporate to dryness on a water bath, and ignite on a gradually rising temperature. Finish the ignition on a blast;[8] weigh as stannic oxide—SnO_2.

Tin is sometimes separated from its solutions by evaporating the solution to dryness with nitric acid. The tin is thus converted into the insoluble metastannic acid.

Errors.—There are several objections to this process The great difficulty is involved in the washing of the precipitate. If iron be present in the solution, the precipitate, after washing, is almost sure to be contaminated with appreciable quantities of iron oxide.[9] Other oxides may also contaminate the precipitate. Antimony hydroxide, for example, may be nearly all precipitated with the tin. Hoffmann[10] thinks that an insoluble tin antimoniate—$3SnO_2 . 2SbO_2$—is formed. Arsenic also is precipitated, probably as tin arsenate[11]—$2SnO_2 . As_2O_5$—a reaction which Hoffmann has suggested for the gravimetric determination of arsenic. Lepéz and Storch (*l.c.*) have shown that bismuth too, if present in considerable quantities, will contaminate the precipitated stannic oxide.

Hence, in a general way, *avoid the determination of tin by separating the tin*

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[1] J. J. Berzelius, *Ann. Chim. Phys.* (1), **87.** 50, 1813; R. Engel, *Compt. Rend.*, **124.** 766, 1897; **125.** 464, 651, 709, 1897; C. F. Barfoed, *Zeit. anal. Chem.*, **7.** 260, 1868; J. W. Mellor, *Modern Inorganic Chemistry*, London, 791, 1912.

[2] D. B. Dott, *Pharm. Journ.* (4), **27.** 486, 1908.

[3] J. Löwenthal, *Journ. prakt. Chem.* (1), **56.** 366, 1852.

[4] If stannous chloride be present, oxidise with bromine or chlorine water.

[5] Or sodium sulphate. H. Rose (*Pogg. Ann.*, **112.** 164, 1861; *Chem. News*, **5.** 87, 1862) used sulphuric acid for the precipitation.

[6] To make sure all the tin is precipitated, add a few drops of the clear solution to a hot solution of ammonium nitrate or sodium sulphate. If all the tin is precipitated, no further precipitation will occur.

[7] If washed with boiling water, a turbid filtrate may be produced. R. Bunsen's plan (*Liebig's Ann.*, **106.** 13, 1858) of washing with ammonium acetate or ammonium nitrate removes this difficulty. For the colloidal stannic acids, see J. M. van Bemmelen, *Zeit. anorg. Chem.*, **23.** 124, 1900. M. Liebschutz (*Chem. News*, **102.** 213, 1910) adds a dilute solution of albumen to the solution from which the colloidal metastannic acid is to be precipitated, and heats the solution for a short time. The stannic acid is entangled with the albumen as the latter curdles. The curd is filtered at once. Any copper, etc., entangled with the tin is removed by boiling the solution with dilute nitric acid. The method is also recommended for the sulphides of zinc, lead, etc. Paper pulp acts well with this and similar precipitates. See also pages 96 and 179.

[8] Mere heating to redness does not suffice to expel all the water—J. B. Dumas. *Liebig's Ann.*, **105.** 104, 1858.

[9] According to H. Rose (*Pogg. Ann.*, **112.** 169, 1835) the iron becomes soluble when the solution is evaporated to dryness. C. Lepéz (*Monats. Chem.*, **10.** 283, 1889) shows that iron, chromium, and cerium lead to the incomplete precipitation of metastannic acid in dilute nitric acid solutions; while aluminium, uranium, cobalt, nickel, and copper do not. F. H. van Leent (*Monit. Scient.* (4), **12.** 866, 1899; *Chem. News*, **78.** 320, 1898) states that chromium and aluminium, as well as iron, retard the precipitation of metastannic acid.

[10] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 45, 1910.

[11] E. Haeffely, *Phil. Mag.* (4), **10.** 220, 1855.

as stannic acid by the action of nitric acid, etc., since the stannic oxide may be contaminated with silica, phosphates, arsenates, antimoniates, lead, bismuth, ferric oxides, etc.

§ 143. The Precipitation of Tin as Sulphide.

The precipitation of tin by metallic zinc is much easier than the usual process of separation by precipitation as sulphide or hydroxide and weighing as stannic oxide. Whenever convenient, analysts avoid the precipitation of tin both as sulphide and hydroxide (stannic acid).

Precipitation of Tin Sulphide.—The combined filtrates containing the tin are neutralised with ammonia, acidified with acetic acid, and saturated with hydrogen sulphide. The stannic sulphide is but very slightly soluble in acetic acid solution containing oxalates.[1] Let the precipitate stand in a warm place over-night.[2] Decant the clear liquid through a Gooch's crucible, and wash the precipitate four or five times by decantation with a solution of ammonium nitrate or acetate.[3] Finally transfer the precipitate to the crucible and wash free from chlorides.

Conversion of Sulphide into Oxide.[4]—Dry the Gooch's crucible, and heat the crucible very gently in its saucer with free access of air until the smell of sulphur dioxide is no longer perceptible.[5] If the temperature be raised too rapidly, at this stage fumes of stannic sulphide would be evolved and burnt to stannic oxide, consequently giving low results. The crucible should be covered with a lid to prevent loss by decrepitation during the earlier stages of the ignition. Remove the lid, and raise the temperature gradually with free access of air. Finish off by blasting the crucible for half an hour. Cool the crucible in a desiccator.

Removal of Sulphates.—The stannic oxide—SnO_2—so formed holds a little sulphuric acid[6] very tenaciously. Hence, weigh the crucible. Place a piece of ammonium carbonate—about half a centimetre diameter—in the crucible, and blast it again. This treatment with the ammonium carbonate is repeated until two successive weighings do not differ by more than 0·0005 grm.[7]

The result is generally a little too high because of the adsorption of alkalies mentioned above, and the difficulty which attends the complete conversion of tin sulphide to tin oxide. A little sulphate also is nearly always retained by the oxide. As a consequence of these facts, *the gravimetric determination of tin as sulphide is employed as little as possible.*[8] Electrolytic or volumetric processes are far more satisfactory.

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[1] If Clarke and Henz's process has been used, the solution contains ammonium oxalate and tartrate. These exert an appreciable solvent action on the tin sulphide. Another reason for condemning the gravimetric process. Clarke (page 208) destroyed the organic acids by means of potassium permanganate before precipitating the tin as sulphide. G. W. Wdowiszewski (*Stahl Eisen*, **27**. 781, 1907) destroys organic matter (tartaric acid) by digesting the solution in a covered beaker with 50 c.c. nitric acid (sp. gr. 1·4) and 10 c.c. of sulphuric acid (sp. gr. 1·65). The solution is evaporated on a sand-bath down to about 30 c.c. The black or brown mass becomes almost colourless when mixed with 20 c.c. nitric acid. In the case of tin, of course, stannic oxide would be precipitated by this treatment.

[2] The tin sulphide is a difficult precipitate to deal with, because it separates in a slimy condition, especially if the solution be boiled during the passage of the gas. The slimy precipitate also retains alkaline salts very tenaciously, and is difficult to wash, particularly in the absence of ammonium salts. See page 96.

[3] R. Bunsen, *Liebig's Ann.*, **106**. 13, 1858.

[4] J. Löwenthal, *Journ. prakt. Chem.* (1), **56**. 366, 1852.

[5] For the volatilisation of stannic sulphide during the roasting, see C. J. Brooks, *Chem. News*, **73**. 218, 1896.

[6] That is, sulphates derived from the oxidation of the sulphide. F. Henz, *Zeit. anorg. Chem.*, **37**. 39, 1903.

[7] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 284, 1851.

[8] It is generally used when but minute traces have to be determined.

§ 144. The Volumetric Determination of Tin—Mène's Ferric Chloride Process.

This method is founded upon the fact that tin sulphide can be dissolved in hydrochloric acid, and the resulting stannic chloride reduced to stannous chloride by means of an excess of metallic iron.[1] The solution of stannous chloride is then titrated with a standard ferric chloride solution,[2] which oxidises the stannous chloride back to stannic chloride: $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$.[3]

Dissolution of the Tin.—If other metals are present, the strongly acid solution is reduced by warming it at 80° or 90° with a piece of iron wire, when lead, arsenic, antimony, copper, and bismuth, if present, are precipitated. The solution is filtered, and neutralised with thin strips of zinc, whereby tin and lead are precipitated. When the action is over and a drop of the clear filtrate gives no reaction for tin with "hydrogen sulphide water," pour off the clear liquid and wash the residue twice by decantation so as to keep the precipitated metals in the flask.[4]

The Titration.—Add 150 c.c. of hydrochloric acid (sp. gr. 1·16), and protect the contents of the flask from oxidation by a trap (page 188). Heat the solution to boiling,[5] and when everything is dissolved, titrate with the standard solution of ferric chloride. The titration should be conducted rapidly, since the stannous chloride is very sensitive to oxidising agents, oxygen dissolved in the water, etc.[6] The end of the reaction is indicated when a drop of ferric chloride imparts a permanent pale yellow tinge to the solution.

The End Point.—F. Mohr, one of the pioneers in volumetric analysis,[7] says that, "in Mène's process, the coloration of the solution by the ferric chloride is not sufficiently marked to enable the operator to recognise with certainty if a drop be added in excess." With moderately concentrated solutions, a person with normal colour vision will soon recognise the effect when one drop of the ferric chloride has been added in excess, but with dilute solutions of ferric chloride Mohr's objection is quite valid. However, Morgan[8] has shown that if a blue Bunsen's flame be examined by looking through the solution being titrated, it will appear to have a greenish colour as soon as a trace of ferric chloride is in the solution. Morgan claims that a solution containing the equivalent of 0·00005 grm. of ferric oxide in 25 c.c. of water can be so recognised. The blue flame of a small Bunsen's burner is placed about 13 mm. below the bottom of the flask in which the solution is being titrated. A good clear glass flask must be used, and the titration conducted in a darkened room, or in a dark corner.

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[1] C. Mène, *Compt. Rend.*, **31**. 82, 1850; *Dingler's Journ.*, **117**. 230, 1850; K. Pellet and A. Allart, *Bull. Soc. Chim.* (2), **27**. 43, 438, 1877; J. A. Sanchez, *ib.* (4), **7**. 890, 1910; H. Nelsmann, *Zeit. anal. Chem.*, **16**. 50, 1877; H. J. B. Rawlins, *Chem. News*, **107**. 53, 1913.

[2] STANDARD FERRIC CHLORIDE.—Dissolve, say, 37 grms. of piano wire in hydrochloric acid and dilute the solution to a litre. Or evaporate 90 grms. of pure commercial ferric chloride to dryness with hydrochloric acid; dissolve the residue in 150 c.c. of hydrochloric acid, and make the solution up to a litre. Standardise by dissolving a gram of pure tin in hydrochloric acid as indicated for tin in the text. Oxidise with nitric acid or hydrogen peroxide; evaporate twice to dryness, and dissolve in 200 c.c. of hydrochloric acid. Make the solution up to a litre.

[3] This is the converse of J. Löwenthal and A. Stromeyer's process for iron (R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1**. 365, 1875).

[4] If no zinc is present, add a small piece to fill the flask with an atmosphere of hydrogen.

[5] Do not boil too vigorously, or the hydrochloric acid will be weakened in strength before all the tin is dissolved.

[6] A. C. Campbell, *Journ. Anal. App. Chem.*, **2**. 287, 1888.

[7] F. Mohr, *Lehrbuch der chemisch-analytischen Titrirmethode*, Braunschweig, 264, 1874.

[8] F. H. Morgan, *Journ. Anal. App. Chem.*, **2**. 169, 1888; C. L. H. Schwarz (*Praktische Anleitung zu Maassanalysen*, Braunschweig, 132, 1853) added a drop of potassium thiocyanate to the solution and titrated until a persistent red tint appeared; C. Victor (*Chem. Ztg.*, **29**. 179, 1905) titrates until starch and potassium iodide indicator is blued.

Errors.—Mohr also points out that "Mène has stated, but not proved, that the decomposition is complete. A reverse action between the stannic chloride and the ferrous chloride proceeds very slowly in the cold, and is more marked on boiling. The reaction is only complete if an appreciable excess of ferric chloride be present. On the other hand, ferric chloride is wholly reduced by an equivalent quantity of stannous chloride; but stannous chloride cannot be oxidised by an equivalent, but only by an excess of ferric chloride." As a matter of fact, the results are very good when the precautions are taken to prevent oxidation of the stannous chloride either during or before the titration. Molybdenum, antimony, titanium, and tungsten interfere with the ferric chloride titration; uranium does not interfere. The titration in the presence of uranium wants careful watching, since the uranous salts are peroxidised *after* the tin and form a yellow solution. The ferric chloride tint gradually fades as the uranium is peroxidised. Rawlins obtained a maximum error of 0·15 per cent. by the process.

Löwenthal and Stromeyer's Process.—Owing to the difficulty in determining the end point when the more dilute ferric chloride solutions are employed, many prefer the Löwenthal modification,[1] where an excess of the standard ferric chloride is added to the solution. The stannous chloride reduces part of the ferric to ferrous chloride. The amount of ferrous chloride so reduced is determined by the permanganate titration—Reinhardt's process, page 452. The chemical equation $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$ corresponds with the fact that 1 grm. of potassium permanganate represents 2·3888 grms. of stannic oxide—SnO_2—in the given solution.

§ 145. Lenssen's Volumetric Iodine Process for Tin.

In Lenssen's iodine process,[2] the stannous chloride is titrated in an alkaline[3] solution with a standard solution of iodine. The results are usually very slightly low. This is due to the action of air on the stannous chloride, and it is generally considered best to work with acid solutions, which do not oxidise so readily as alkaline solutions. The reaction is generally represented by the equation:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI.$$

This is supposed by Young to take place in two stages: (1) $2SnCl_2 + 4I = SnCl_4 + SnI_4$, when an excess of stannous chloride is present; and (2), the reduction of stannic iodide to stannous iodide by the stannous chloride—$SnI_4 + 2SnCl_2 = 2SnI_2 + SnCl_4$. If too much hydrochloric acid be present, the results will be high owing to the action of the acid on the potassium iodide. The solution should contain about one-fifth its volume of concentrated hydrochloric acid (sp. gr. 1·16). Sulphates, phosphates, iodides, bromides, iron, nickel, cobalt, zinc, manganese, molybdenum, tungsten, titanium, uranium, aluminium, lead, chromium, and bismuth do not interfere with the results unless their colour is sufficient to mask the colour of the indicator—starch blue. Arsenic spoils the result. According to Sanchez, the presence of antimonious chloride, $SbCl_3$, does no harm. If copper be present, the iodine must be added slowly, and the solution briskly agitated, otherwise the results will be too high. When copper is present, one-third the volume of hydrochloric acid should be present, instead of one-fifth.

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[1] J. Löwenthal, *Journ. prakt. Chem.* (1), **76**. 484, 1859; A. Stromeyer, *Liebig's Ann.*, **117**. 261, 1861; C. Zengelis (*Ber.*, **34**. 2046, 1901) titrates the excess of ferric chloride with stannous chloride until a drop of the solution colours a drop of ammonium molybdate blue; and T. Moore (*Chem. News*, **67**. 267, 1893) titrates the excess of ferric chloride with cuprous chloride.

[2] G. de Claubry, *Compt. Rend.*, **23**. 101, 1846; J. A. Müller, *Bull. Soc. Chim.* (3), **25**. 1002, 1901; *Chem. News*, **85**. 114, 1902; A. Fraenkel and J. Fasal, *Mitt. K. K. Tech. Gew. Wien*, **7**. 227, 1897; A. Scheurer-Kestner, *Chem. News*, **4**. 101, 192, 1861; F. Ibbotson and H. Brearley, *ib.*, **84**. 167, 1901; E. Lenssen, *Journ. prakt. Chem.* (1), **78**. 200, 1859; *Liebig's Ann.*, **114**. 114, 1860; G. Topf, *Zeit. anal. Chem.*, **26**. 163, 1887; C. Friedheim, *Zeit. anorg. Chem.*, **4**. 145, 1893; W. H. Low, *Journ. Amer. Chem. Soc.*, **29**. 66, 1907; S. W. Young and M. Adams, *ib.*, **19**. 515, 1897; S. W. Young, *ib.*, **19**. 845, 851, 1897; **23**. 21, 119, 453, 1901; R. Job, *Journ. Soc. Chem. Ind.*, **17**. 325, 1898; T. Benas, *Zur massanalytischen Bestimmung des Zinns und über einige Zinnoxydulsalze*, Berlin, 1884; J. A. Sanchez, *Bull. Soc. Chim.* (4), **7**. 890, 1910; H. J. B. Rawlins, *Chem. News*, **107**. 53, 1913; A. Fränkel and J. Fasal, *ib.*, **78**. 100, 1898; A. Jolles, *Chem. Ztg.*, **12**. 597, 1888.

[3] In the presence of potassium sodium tartrate and sodium bicarbonate.

Reduction of the Stannic to Stannous Chloride.—The hydrochloric acid solution containing the stannic chloride is evaporated to about 50 c.c. in a wide 400-c.c beaker. A piece of clean iron wire[1] is placed in the solution against the side of the beaker, and the whole covered by a watch-glass. The solution is warmed to 80° or 90° on a sand bath or quartz plate. In about half an hour the arsenic, antimony, and copper will be precipitated, and the stannic chloride reduced to stannous chloride.[2] Cool the beaker in a stream of water; wash the clock-glass, etc., rapidly in a stream of cold, recently boiled distilled water.[3]

The Titration.—Add a few drops of starch paste (page 286) to the solution, and titrate the mixture rapidly with a standard solution of iodine[4] until the blue colour of the starch appears. For details of the "iodine" titration, see page 353. Ibbotson and Brearley's test analyses with the powdered "antimony reduction" show :—

Tin used	0·1750	0·1000	0·0480	0·0200	0·0080 grm.
Tin found	0·1752	0·0997	0·0490	0·0201	0·0083 grm.

Rawlins obtained a maximum error of 0·10 per cent. by the process. In all volumetric processes for tin, there is a tendency to low results owing to the rapidity with which the reduced tin salt is oxidised.[5]

§ 146. Henz and Classen's Electrolytic Process for Tin.

Tin is readily deposited from solutions of ammonium oxalate in the presence of an excess of oxalic acid.[6] If ammonium oxalate be used alone, it is converted during the electrolysis into ammonium carbonate. The electrolyte then smells of ammonia, and stannic acid may separate, particularly if much tin be present. The stannic acid is dissolved by an excess of oxalic acid. Hence the electrolyte must always be kept acid by the addition of, say, oxalic acid.

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[1] C. and J. J. Beringer (*A Textbook of Assaying*, London, 288, 1906) recommend inserting a piece of nickel foil 20 cm. long and 5 cm. wide coiled on itself to form a cylinder into boiling solution for the reduction. F. Ibbotson and H. Brearley (*Chem. News*, **84.** 167, 1901) prefer reducing the stannic chloride to the stannous condition by boiling the solution with powdered antimony. Cool in an atmosphere of CO_2 (fig. 127, page 298), and titrate without removing the excess of antimony. J. A. Sanchez (*Bull. Soc. Chim.* (4), **7.** 890, 1910) reduces with aluminium wire added in small portions until all is dissolved. D. B. Dott, *Pharm. Journ.* (4), **27.** 486, 1908.

[2] The assumption is justified in practice, although there is no convenient test.

[3] The black precipitate—antimony, arsenic, and copper if present—does not interfere with the result. Antimony precipitated by iron does *very slowly* reduce stannic chloride, and therefore the "starch blue" obtained in the titration is not quite permanent. Antimony which has been fused, cooled, and ground in an agate mortar has a scarcely perceptible reducing action in the cold, although it very quickly reduces a boiling solution. Hence Ibbotson and Brearley's process of reduction indicated in a preceding footnote. When the solution has cooled in an atmosphere of CO_2, there is no need to remove the excess of antimony for the titration.

[4] Page 288. About 21·32 grms. of iodine and 45 grms. of potassium iodide are made up to a litre. One c.c. of this solution will represent nearly 0·01 grm. of tin. The solution should, however, be standardised against a known weight of tin.

[5] E. A. Lewis, *London Min. Journ.*, 606, 1911.

[6] F. Henz, *Zeit. anorg. Chem.*, **37.** 31, 1903; A. Fischer, *ib.*, **42.** 363, 1904; J. M. M. Dormaar, *ib.*, **53.** 349, 1907; A. Classen and O. Bauer, *Ber.*, **16.** 1061, 1883; A. Classen and M. A. von Reis, *ib.*, **14.** 1622, 1881; A. Classen, *ib.*, **17.** 2467, 1884; **18.** 1110, 1885; **27.** 2060, 1894; M. Heidenreich, *ib.*, **28.** 1586, 1895; C. Engels, *Zeit. Electrochem.*, **2.** 418, 1896;

The Electrolyte.—In gravimetric analysis the tin is obtained as sulphide, and it is usually dissolved in sodium sulphide. To convert this solution into acid oxalate, acidify the solution with dilute acetic acid. Dissolve equal parts of ammonium oxalate and oxalic acid in hot water, so that the total amount of oxalate and oxalic acid per 0·1 grm. of tin amounts to 3·5 grms. Heat the solutions to boiling and pour the oxalate solution into the tin solution. The resulting solution may be slightly turbid owing to the separation of some sulphur, but it forms an excellent electrolyte for the deposition of tin.

The Electrolysis.—Use a current density of about 0·2 to 0·3 amp., and an E.M.F. of 2 to 3 volts. In about six hours most of the tin will have deposited. Add 8 c.c. of sulphuric acid (1 : 1) (or add more oxalic acid), and continue the electrolysis for another twenty-four hours. All the tin will then probably be precipitated.[1] Engels says that the electrolysis can be shortened by the addition of hydroxylamine sulphate to the electrolyte (see page 261).

Results.—The tin is precipitated as a compact shining silver-white metal. It is washed, dried, and weighed in the usual manner. In illustration of the results, Henz gives the subjoined numbers :—

Table XLIX.—Test Analyses with the Electrolytic Process for Tin.

Used Sn. Grm.	Current density. Amp.	Ammonium oxalate. Grms.	Sulphuric acid added.		Total duration of the electrolysis. Hrs.	Found Sn. Grm.	Error.	
			After hours.	c.c.			Grm.	Per cent.
0·1017	0·75–1·00	15	5½	10	28	0·1036	+0·0019	1·7
0·1017	0·48–0·05	15	3	10	27	0·1021	+0·0004	0·4
0·2555	0·35–0·24	15	7	10	24	0·2555	0·0000	0·0
0·2555	0·38–0·20	15	8	10	24	0·2548	−0·0007	0·3
0·2555	0·30–0·10	15	7½	10	23	0·2550	−0·0005	0·2
0·2555	0·38–0·20	30	3	5	22	0·2551	−0·0004	0·2
0·1017	0·15–0·10	15	6	2	21	0·1016	−0·0001	0·1

This table shows that the proportions indicated above are likely to give satisfactory results. The time factor is a rather serious objection.

Removal of Tin from the Electrode.—There is a difficulty in removing tin from the cathode, since the metal does not readily dissolve in acids—even boiling hydrochloric acid dissolves the metal very slowly. Nitric acid forms a coating of stannic oxide, which must be frequently removed in order to expose a fresh surface of the metal to attack. Classen recommends warming the deposit with a mixture of 2 grms. of tartaric acid, 8 c.c. of water, and 2 c.c. of concentrated

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A. Scheen, *ib.*, **14**. 257, 1908 ; F. Förster and J. Wolf, *ib.*, **13**. 205, 1907 ; H. J. S. Sand, *ib.*, **13**. 327, 1907 ; H. Ost, *Zeit. angew. Chem.*, **10**. 325, 1897 ; **14**. 817, 1901 ; A. Hollard, *Bull. Soc. Chim.* (3), **29**. 262, 1903 ; A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911 ; A. H. Cushman and E. B. Wettengel, *Journ. Ind. Eng. Chem.*, **5**. 217, 1913.

[1] To make sure, withdraw about 1 c.c. by means of a pipette ; acidify the solution with sulphuric acid, add "H_2S water," and warm gently. If yellow or brown stannous or stannic sulphides separate, the electrolysis is not completed. Do not confuse free sulphur with tin sulphide.

nitric acid; or fusion with potassium bisulphate. Some recommend coating the cathode with a film of copper of silver before precipitating the tin in order to prevent the platinum being seriously attacked during the subsequent removal of the deposited tin. Another plan is to make the dish the anode and electrolyse a solution of dilute sulphuric acid with a piece of copper wire as cathode.

§ 147. The Evaluation of Commercial Compounds containing Tin.

Tin Oxide.—The amount of tin oxide can be determined by reducing the sample to metal in a current of hydrogen or coal gas (page 268), and dissolving the metal in hydrochloric acid. The solution may be titrated for tin as indicated above. The metal may also be obtained by reduction with potassium cyanide (page 269). The button of metal should be specially analysed for tin, since it may be contaminated with other metals.

Tin Ash (*Calcine*).—Here, tin and lead are to be separated. The hydrochloric acid solution is treated with an excess of sodium hydroxide, and saturated with hydrogen sulphide. Lead is precipitated; tin remains in solution. The tin solution may be treated as indicated, pages 307–309; the lead sulphide as on page 320.[1]

Sodium Stannate.—Commercial sodium stannate may contain relatively large quantities of sodium arsenate.[2] The analyst may thus have to determine both the tin and the arsenic. The arsenic may be precipitated by placing best piano wire in the solution acidified with hydrochloric acid, as in the case of antimony by Tookey's process. The tin can be determined in the filtrate. The sodium can be determined as chloride by applying part of the process (page 224).

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[1] For the solubility of lead sulphate in stannous chloride, see M. de Jong, *Zeit. anal. Chem.*, **41**. 596, 1901; A. van Raalte, *ib.*, **43**. 36, 1903.

[2] E. Haeffely (*Phil. Mag.* (4), **10**. 220, 1855) adds a known excess of arsenic, boils with an excess of nitric acid, weighs the tin as tin arsenate—$2SnO_2 . As_2O_5$—and determines the excess of arsenic in the filtrate. See T. Goldschmidt, *Dingler's Journ.*, **162**. 77, 1861; A. Scheurer-Kestner, *Rep. Chim. App.*, **4**. 221, 1862; P. T. Austen, *Amer. Chem. Journ.*, **5**. 210, 1883.

CHAPTER XXIV.

THE DETERMINATION OF LEAD.

§ 148. The Properties of Lead Sulphate.

LEAD is perhaps most frequently separated and weighed as sulphate. Lead sulphate is a heavy white powder sparingly soluble in water: 100 c.c. of water dissolve nearly 0·0038 grm. lead sulphate.[1] The solubility is decreased in the presence of small quantities of sulphuric acid, and increased in more concentrated solutions, as well as in solutions of hydrochloric and nitric acids. This is illustrated by the following table:—[2]

Table L.—Solubility of Lead Sulphate in Mineral Acids.

Sulphuric acid.		Hydrochloric acid.		Nitric acid.	
Grm. $PbSO_4$ per 100 grms. sol.	Approximate normality of acid.	Grm. $PbSO_4$ per 100 grms. sol.	Approximate normality of acid.	Grm. $PbSO_4$ per 100 grms. sol.	Approximate normality of acid.
0·003	27	0·33	3	0·14	2
0·011	31	0·59	5	0·35	3
0·039	36	0·78	10	0·95	5

The effect of sulphuric acid in reducing the solubility of lead sulphate is illustrated by the graph, fig. 129. It is generally supposed that lead sulphate is best precipitated from a liquid approximately N-H_2SO_4, and the precipitate is best washed with an acid of the same strength. The solubility of lead sulphate is also reduced in the presence of alcohol. Hence, many prefer to dilute the liquid with two or three times its volume of alcohol or methylated spirit, and wash with a dilute alcoholic solution of sulphuric acid containing 10 per cent. of alcohol and 1 per cent. of sulphuric acid, in order to reduce the loss of lead sulphate to a minimum. There is little difference in the actual results with the alcohol and the dilute sulphuric acid treatments, but the use of alcohol is apt to give high results, because very few sulphates are readily soluble in alcohol. According to Sehnal, lead sulphate is "absolutely insoluble in water containing one part of H_2SO_4 per 1000 c.c." If "absolutely" here means that "the amount of soluble lead sulphate cannot be determined by ordinary analytical methods," I quite agree.

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[1] H. C. Dibbits, *Zeit. anal. Chem.*, **13**. 139, 1874; F. Kohlrausch, *Zeit. phys. Chem.*, **50**. 356, 1905; W. Böttger, *ib.*, **46**. 602, 1903; R. Fresenius, *Liebig's Ann.*, **59**. 125, 1876; G. F. Rodwell, *Chem. News*, **11**. 50, 1865; M. Pleissner, *Ueber die Loslichkeit einiger Bleiverbindungen in Wasser*, Berlin, 1903.

[2] G. F. Rodwell, *Journ. Chem. Soc.*, **15**. 59, 1862; C. S. Sellack, *Pogg. Ann.*, **133**. 137, 1868; *Zeit. anal. Chem.*, **9**. 464, 1870; H. Struve, *ib.*, **9**. 34, 1870; W. Städel, *ib.*, **2**. 180, 1863; C. Stammer, *Dingler's Journ.*, **165**. 209, 1862; *Chem. Ztg.*, **6**. 63, 1884; J. Sehnal, *Compt. Rend.*, **148**. 1394, 1909; K. Beck and P. Stegmüller, *Arb. Kais. Gesund. Amt.*, **34**. 446, 1910.

The solubility of lead sulphate is increased in the presence of alkaline chlorides and many other salts; and it is fairly soluble in ammonium acetate,[1] tartrate, citrate, chloride, nitrate, etc., and in sodium thiosulphate, sodium acetate, caustic alkalies, etc.[2] In illustration, the following table represents the solubility of lead sulphate in ammonium acetate (Noyes and Whitcomb) and in sodium acetate (Dunnington and Long). The solubility is increased by raising the temperature.

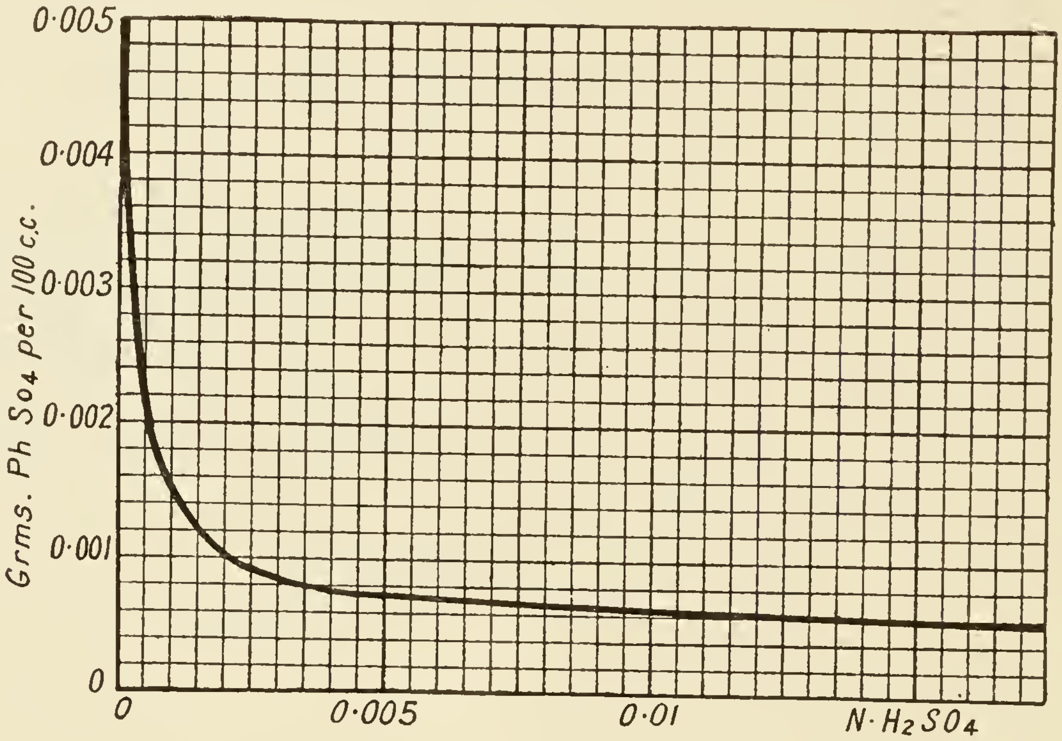

Fig. 129.—Effect of sulphuric acid on the solubility of lead sulphate.

Table LI.—Solubility of Lead Sulphate in Ammonium and Sodium Acetates.

Ammonium acetate.				Sodium acetate.	
25°		100°			
Grm. $PbSO_4$ per 100 c.c.	Grm. acetate per 100 c.c.	Grm. $PbSO_4$ per 100 c.c.	Grm. acetate per 100 c.c.	Grm. $PbSO_4$ per 100 c.c.	Grm. acetate per 100 c.c.
0·0041	0·000	7·12	28	2·05	0·054
0·0636	0·798	9·88	32	8·20	0·9
0·138	1·596	10·58	37	41	11·2
0·302	3·192	11·10	45	...	...

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[1] H. C. Dibbits, *Bull. Soc. Chim.* (2), **20**. 258, 1873; F. P. Dunnington and J. C. Long, *Amer. Chem. Journ.*, **22**. 217, 1899; E. Lenssen, *Journ. prakt. Chem.* (1), **85**. 89, 1862; J. Löwenthal, *ib.* (1), **60**. 267, 1853.

[2] L. Kahlenberg, *Zeit. phys. Chem.*, **17**. 577, 1895; *Chem. News*, **1**. 152, 1860; J. Löwe, *Journ. prakt. Chem.* (1), **74**. 348, 1858; A. A. Noyes and W. H. Whitcomb, *Journ. Amer. Chem. Soc.*, **27**. 747, 1905.

It is therefore necessary to precipitate lead sulphate from solutions as free as possible from ammonium salts, alkaline chlorides, nitric and hydrochloric acids, etc. If potassium salts be present, Levol[1] has pointed out that there is a danger of precipitating potassium sulphate with the lead sulphate in the form of a double lead and potassium sulphate—$K_2Pb(SO_4)_2$. There is not the same risk with sodium sulphate.

The solubility of lead sulphate in sodium thiosulphate and ammonium acetate solutions is frequently employed in separating lead sulphate from barium sulphate. The latter is supposed to be insoluble in ammonium acetate and sodium thiosulphate. When the latter is used, the temperature must be kept below 68°, or an insoluble lead sulphite may be formed. If basic iron sulphate[2] or barium sulphate[3] be precipitated with the lead sulphate, there is a difficulty in dissolving the last traces of the lead sulphate in ammonium acetate, thus leading to low results. With ammonium acetate, there is a small error owing to the slight solubility of barium sulphate in this menstruum. Kernot,[4] for example, finds that at 25°, 0·133 grm. of barium sulphate dissolves in a litre of a solution of ammonium acetate containing 300 grms. of the salt. Solutions of carbonates, but not bicarbonates,[5] convert lead sulphate at ordinary temperatures into lead carbonate, which is soluble in dilute nitric acid, and this reaction is also sometimes used for separating lead sulphate from barium sulphate (see page 515), which does not react with carbonates in the same way.

Lead sulphate is practically unaltered when exposed to the air, and also when ignited at a low red heat. It fuses at 848° without decomposition, provided reducing agents be absent.[6] If heated for a long time, there may be an appreciable loss by volatilisation.[7] Thus, 1·4082 grms., when heated in a porcelain tube in a current of carbon dioxide, lost in weight, according to Williams, 0·134 per cent. either by volatilisation or partial decomposition.

§ 149. The Determination of Lead as Sulphate.

The solution, if dilute, is concentrated by evaporation, and if hydrochloric or nitric acids be present, the solution is evaporated with about 1 c.c. of sulphuric acid[8] (1 : 1) until copious fumes of sulphuric acid are evolved. This drives off the nitric and hydrochloric acids, which interfere with the subsequent precipitation of the lead sulphate. Cool the solution. Add water until the volume of the liquid is about 50 c.c. and the solution contains between 1 and 2 per cent. of H_2SO_4—about $\frac{1}{2}N\text{-}H_2SO_4$. Filter the solution through filter paper, or through a Gooch's crucible packed with asbestos, or, better still, through a Munroe's crucible,[9] since there is a risk of the acid attacking asbestos. Wash the precipitate with dilute sulphuric acid ($\frac{1}{2}$N- to N-H_2SO_4),[1] and finally with alcohol, until the washings are free from sulphuric acid.[2] Dry the precipitate at 100°. Ignite the precipitate over the full flame of a Méker's burner,[3] and, when cold, weigh the ignited precipitate as lead sulphate—$PbSO_4$. The weight of the lead sulphate multiplied by 0·7359 represents the corresponding amount of lead oxide—PbO—or use Table XCIII., or fig. 23. The results are usually excellent.[4]

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[1] A. Levol, *Rép. Chim. App.*, **4.** 21, 1862; *Chem. News*, **5.** 144, 1862; J. J. Fox, *Proc. Chem. Soc.*, **23.** 199, 1907; *Journ. Chem. Soc.*, **95.** 878, 1909; F. G. Belton, *Chem. News*, **91.** 191, 1905.

[2] J H. Walton and H. A. Scholz, *Amer. Chem. Journ.*, **39.** 771, 1908; *Chem. News*, **98.** 61, 76, 1908.

[3] J. C. Bull, *School Mines Quart.*, **23.** 348, 1903; *Chem. News*, **87.** 40, 52, 66, 1903.

[4] G. Kernot, *Rend. Acad. Sci. Napoli* (3), **15.** 155, 1909.

[5] H. Rose, *Pogg. Ann.*, **95.** 426, 1855.

[6] O. L. Erdmann, *Journ. prakt. Chem.* (1), **62.** 381, 1854.

[7] C. P. Williams, *Chem. News*, **23.** 236, 1871; A. Mitscherlich, *Journ. prakt. Chem.* (1), **83.** 485, 1861; J. Boussingault, *Compt. Rend.*, **64.** 1159, 1867.

[8] Be careful in adding concentrated acid to dilute solutions, or some liquid may be lost by spurting.

[9] Filter paper can be used to collect the lead sulphate. In that case, dry the washed precipitate; separate the precipitate from the paper on a watch-glass; burn the paper in a weighed

§ 150. The Separation of Lead from Bismuth, Copper, and Cadmium.

The process just indicated gives excellent separations of lead from copper, cadmium, zinc, etc. We therefore take up the problem left on page 276: the separation of the constituents of the residue left on treatment of the hydrogen sulphide precipitate with sodium monosulphide. The residue is dissolved in concentrated hydrochloric acid. There are two cases:—

(1) *Bismuth absent.*—This is nearly always the case in the analysis of pottery colours and glazes. The solution is evaporated on a water bath along with a little sulphuric acid. The evaporation is completed on a hot plate, or over a ring burner, until the sulphuric acid begins to fume. The object is to drive off the hydrochloric acid, which leads to an imperfect precipitation of the lead sulphate. The lead sulphate is determined by diluting the solution as indicated for lead sulphate (page 317).

(2) *Bismuth present.*—The solution should contain just enough hydrochloric acid to prevent the precipitation of basic bismuth salts when the solution is diluted. The right amount of hydrochloric acid is determined[5] as follows:—Evaporate the solution on a water bath, and put a drop of the evaporating solution on a watch-glass with a drop of water. If no precipitate forms, too much hydrochloric acid *may* be present. Continue the evaporation. If a white precipitate forms, the evaporation has gone too far and hydrochloric acid is added, a few drops at a time, until no precipitate of basic bismuth salt forms, when a drop of the solution is diluted with water. The lead is then precipitated as lead sulphate, and the bismuth separated from the copper and the cadmium by Jannasch's process (page 348). If no bismuth be present, proceed to copper (page 350). The process just indicated for the separation of lead from bismuth, copper, and cadmium requires great care and some practice before good results can be ensured. Some might prefer to employ Löwe's process for the separation of bismuth from copper, cadmium, and lead, and afterwards separate the lead from the copper and cadmium in the form of lead sulphate. The separation of bismuth is discussed on page 347 *et seq.*

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crucible; moisten the ash with nitric acid; add a drop of sulphuric acid; evaporate to dryness on a low flame. Transfer the precipitate from the watch-glass to the crucible, and ignite over the Méker's burner to a constant weight.

[1] L. L. de Koninck (*Bull. Soc. Chim. Belg.*, **21.** 141, 1907) washes the precipitate with water containing 0·7 per cent. of ammonium sulphate.

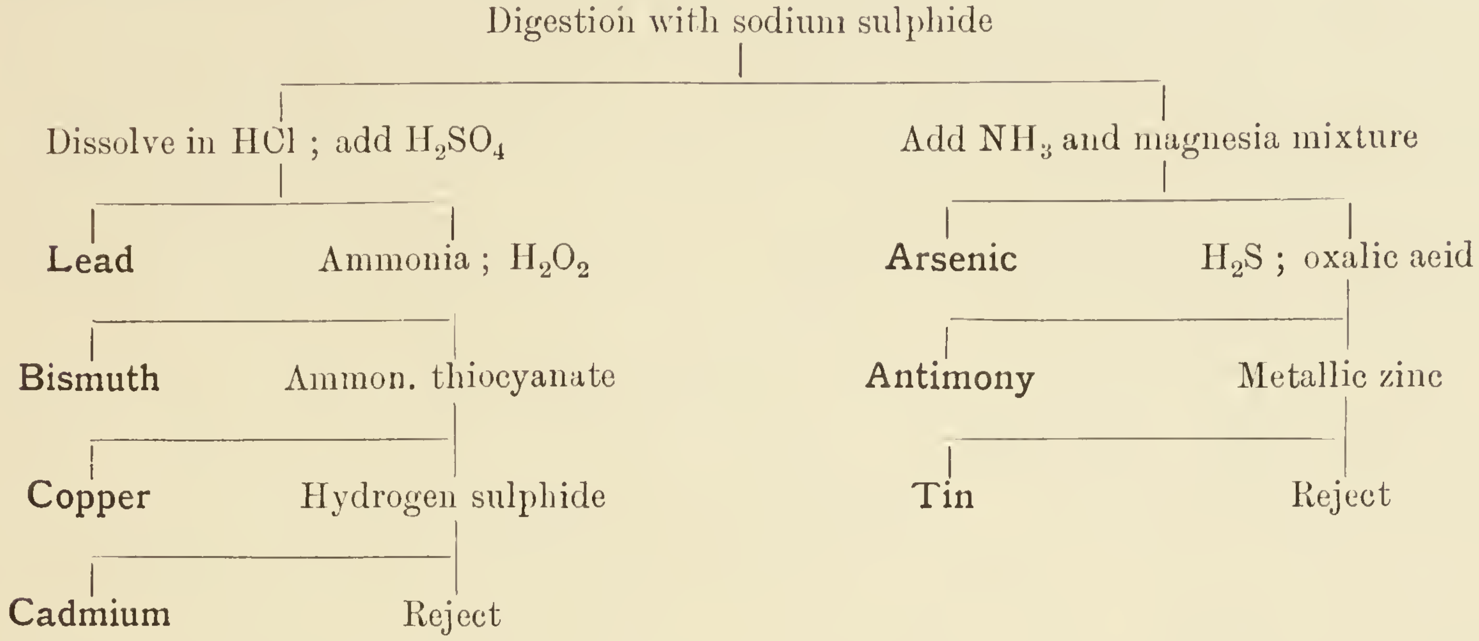
[2] If the sulphuric acid be not washed out, particularly from filter paper, the paper may be charred as the acid becomes more and more concentrated during the drying of the precipitate. With the Munroe's crucible there is not so much need for the alcohol washing.

[3] Some merely dry the precipitate at 110° before weighing.

[4] According to A. G. Blakeley and E. M. Chanee (*Journ. Soc. Chem. Ind.*, **30.** 518, 1911), in the ordinary method of precipitating lead as sulphate, the presence of tin and antimony interfere because basic salts are precipitated with the lead sulphate. P. H. Walker and H. A. Whitman, *Journ. Ind. Eng. Chem.*, **1.** 519, 1909.

[5] O. Steen, *Zeit. angew. Chem.*, **8.** 530, 1895; H. Rose, *Pogg. Ann.*, **110.** 432, 1860; C. Friedheim, *Leitfaden für quantitative chemische Analyse*, Berlin, 300, 1905; H. Herzog, *Journ. Anal. App. Chem.*, **1.** 245, 1887; *Chem. News*, **58.** 129, 1888.

The scheme for separating the constituents of the precipitate produced by hydrogen sulphide may now be conveniently summarised (mercury absent)—solids to left, solutions to right:—



Any step can be omitted if the qualitative process shows the corresponding element is absent. The scheme for dealing with the next group is given on page 386.

§ 151. The Analysis of White Lead.

There are several alternative schemes for the analysis of white lead.[1] The following process brings out the information required from the chemical analysis for most technical operations:—

Hygroscopic Moisture.—Dry a weighing bottle in a steam oven; cool in a desiccator and weigh. Transfer about 10 grms of the sample to the weighing bottle, and weigh again. Dry the sample in the steam or air bath at from 100° to 105° until no further loss in weight occurs—overnight generally suffices—when further heated. The loss in weight represents hygroscopic moisture.[2]

Dissolution of the White Lead.—Transfer a gram of the dried sample to a 100-c.c. flask and boil for 5 minutes with an excess of dilute acetic acid.[3] Filter through a 6·5-cm. filter paper, and wash once with hot dilute acetic acid and then with hot water. The residue may contain insoluble sand (silica), silicates (clays), lead sulphate, barium carbonate, calcium sulphate, and possibly alumina, magnesia, and free lead.

The Soluble Portion.—Heat the solution; add 1 c.c. of a saturated solution of mercuric chloride.[4] Pass hydrogen sulphide through the boiling liquid for about half an hour.[1] Let the precipitate settle. Filter.[2] Wash with hot water.[3] The precipitate might contain zinc and lead sulphides; the filtrate, calcium, barium, and possibly magnesium salts. Boil the filtrate to expel the hydrogen sulphide, and precipitate the barium with sulphuric acid (page 618) and filter. Calculate the corresponding amount of barium carbonate by multiplying the weight of barium sulphate by 0·84555. Precipitate the lime as oxalate (page 213), and calculate the corresponding amount of calcium carbonate by multiplying the weight of calcium oxide by 1·7844. Precipitate the magnesia as phosphate (page 218), and calculate the corresponding amount of magnesium carbonate by multiplying the weight of the magnesium pyrophosphate with the factor 0·7576.

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[1] P. Drawe, *Zeit. angew. Chem.*, **13**. 174, 1902; A. Coppalle, *Ann. Chim. Anal. App.*, **12**. 62, 1907; G. W. Thompson, *Journ. Soc. Chem. Ind.*, **24**. 487, 1905; G. Tissandier, *Chem. News*, **23**. 268, 1871; A. Neujean, *ib.*, **22**. 251, 1870; A. Adriani, *ib.*, **4**. 43, 1861.

[2] W. A. Davis and C. A. Klein (*Journ. Soc. Chem. Ind.*, **26**. 848, 1907) say heat has no action below 110°, and decomposition begins at 120°. L. Joulin (*Chem. News*, **27**. 211, 1873) considers that at temperatures over 50° there is no security against partial decomposition and loss of carbon dioxide. At 150° the pressure of cerusite was below 30 mm.; at 250°, 75 mm.; and at 300° decomposition was complete. I have met with only one sample of white lead which showed an appreciable decomposition when dried in the steam oven, but usually, drying in the steam oven is quite safe.

[3] Dilute Acetic Acid.—10 c.c. of glacial acetic acid with 25 c.c. water. Some prefer dilute nitric acid (1 : 5). If too much nitric acid be present, the lead sulphate is not completely precipitated.

[4] When very small amounts of lead are to be precipitated as sulphide, E. Murmann (*Monats. Chem.*, **19**. 404, 1899; M. Antony and T. Benelli, *Gaz. Chim. Ital.*, **26**. i, 218, 1906) adds mercuric chloride to the solution before passing the gas. This renders the precipitate easy to filter. The mercuric sulphide is volatilised on roasting the precipitate.

The precipitated mixture of zinc and lead sulphides is ignited in a porcelain crucible at a low temperature,[4] in order to burn off the filter paper. Brush the residue into a small 400-c.c. beaker and wash out the crucible by means of dilute nitric acid (1 : 5). Add about 1 c.c. of sulphuric acid (1 : 1); evaporate until copious white fumes of sulphuric anhydride come off; and separate the lead sulphate as described above. Weigh the ignited precipitate of lead sulphate as $PbSO_4$. The weight of the lead sulphate, multiplied by 0·8526, represents the weight of normal white lead—$2PbCO_3 . Pb(OH)_2$—in the given sample. The zinc is precipitated from the cold filtrate as zinc ammonium phosphate (page 366), and the corresponding amount of ZnO or $ZnCO_3$ computed in the usual manner.

The Insoluble Portion.—Boil the residue with 20 c.c. dilute hydrochloric acid (1 : 1) and 5 grms. of ammonium chloride for 5 minutes. Dilute to 400 c.c. Boil 5 minutes. The lead and calcium sulphates are dissolved; barium sulphate,[5] silica, and silicates remain undissolved. Filter and wash with hot water. The lead is precipitated from the filtrate by hydrogen sulphide.[6] The lead sulphide is treated as described above and reported as lead sulphate. The filtrate is treated with ammonia[7] and ammonium oxalate to precipitate the lime as calcium oxalate (page 213). Report as calcium sulphate. The residue (insoluble in ammonium chloride and hydrochloric acid), containing the barium sulphate, sand, and clay, is ignited in a platinum crucible and weighed. Fuse the residue with ten times its weight of sodium carbonate. Extract with water; filter; and wash. Dissolve the precipitate in 5 c.c. of hydrochloric acid; boil; add sulphuric acid to precipitate barium sulphate (page 618); weigh the precipitate; and report as barium sulphate. Deduct this weight from the "insoluble," and report the difference as "clay, sand, and insoluble silicates."

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[1] Calcium chloride in a dilute solution of lead chloride in presence of hydrochloric acid or nitric acid may give no precipitate with hydrogen sulphide owing to the solubility of lead sulphide in presence of calcium chloride and acid. K. H. Mertens, *Pharm. Centr.*, **34.** 273, 1895; H. Hager and E. Geissler, *ib.*, **34.** 273, 1885.

[2] A. Gawalovski (*Zeit. anal. Chem.*, **26.** 51, 1887) suggests saturating the margin of the filter paper with paraffin or other fat (free from ash) in order to prevent the creeping of the precipitate over the edge of the paper.

[3] F. Moldenhauer (*Chem. Ztg.*, **22.** 256, 1898; *Chem. News*, **79.** 182, 1899) washes first with water and then with warm ammonium sulphide.

[4] For the alleged volatilisation of lead sulphide, see H. Rose, *Pogg. Ann.*, **110.** 134, 1860; G. F. Rodwell, *Journ. Chem. Soc.*, **15.** 43, 1863; A. Souchay, *Zeit. anal. Chem.*, **5.** 63, 1886; A. Classen, *Journ. prakt. Chem.* (1), **96.** 257, 1865.

[5] It must be remembered that heavy spar is slightly soluble in nitric acid. Hence, the "insoluble" heavy spar can only be determined approximately, unless the solution be evaporated to dryness, and the residue taken up with water, filtered, washed, and calcined at a low red heat. Note that the "total heavy spar" does not necessarily represent the amount of heavy spar added to the white lead, because the heavy spar used is not usually pure barium sulphate, but contains, say: 90 per cent. $BaSO_4$; 2 per cent. CaO; 7 per cent. SiO_2; 1 per cent. Al_2O_3 and Fe_2O_3. Since different solvents may dissolve different amounts of the heavy spar, it is easy to see how different "total insolubles" may be reported by different analysts. In exact work it is as well to fuse the "insoluble" with sodium carbonate as indicated in the text.

[6] For the precipitation of lead sulphide from hydrochloric acid solutions, the solution should not contain more than 3 or 4 c.c. of hydrochloric acid (sp. gr. 1·12) per 100 c.c. of solution in the cold.

[7] If alumina be precipitated when ammonia is added, filter, wash, ignite, weigh, and report as alumina.

Collecting these results together, it will be seen that we have followed the subjoined scheme:—

- I. Soluble in dilute acetic acid. Treat with H_2S.
  - A. Soluble. Add sulphuric acid.
    - (*a*) Soluble. Add ammonium oxalate.
      - 1. Soluble. Add microcosmic salt.
        - (i.) Soluble. Reject.
        - (ii.) Insoluble Mg salt . . . . . $MgCO_3$.
      - 2. Insoluble Ca salt . . . . . . $CaCO_3$.
    - (*b*) Insoluble barium sulphate . . . . . . $BaCO_3$.
  - B. Insoluble. Take up with HNO_3, add H_2SO_4.
    - (*a*) Soluble. Add microcosmic salt.
      - 1. Soluble. Reject.
      - 2. Insoluble Zn Salt . . . . . . ZnO.
    - (*b*) Insoluble Pb salt . . . . $2PbCO_3 . Pb(OH)_2$.
- II. Insoluble. Digest with HCl and NH_4Cl.
  - A. Soluble. Pass H_2S.
    - (*a*) Soluble. Add ammonium oxalate.
      - 1. Soluble. Reject.
      - 2. Insoluble Ca salt. . . . . . . $CaSO_4$.
    - (*b*) Insoluble Pb salt . . . . $PbSO_4$.
  - B. Insoluble. Weigh, fuse sod. carb., etc.
    - (*a*) Soluble. Add H_2SO_4.
      - 1. Soluble. Reject.
      - 2. Insoluble Ba salt . . . . $BaSO_4$.
    - (*b*) Insoluble. Subtract weight of II. B., (*a*) 2, from II. B., Insolubles.

Carbon dioxide can be determined as indicated on page 553.

Water is determined as indicated on page 561 or 574.

Iron is determined by dissolving 5 grms. of the original sample in dilute nitric acid. Precipitate the lead as sulphate; filter; evaporate to dryness; dissolve the residue in 1 c.c. of hydrochloric acid and a little water; and make the solution up to 200 c.c. Determine the iron colorimetrically[1] (page 200) in one 100 c.c.

Copper is determined colorimetrically by the ammonia process (page 355) in the 100 c.c. remaining after the iron has been determined.

Acetic acid is determined by alternate distillation and distillation in steam from a mixture of the sample with phosphoric acid.[2] The distillate is titrated with $\frac{1}{10}$N-NaOH and phenolphthalein as indicator until 10 c.c. of the distillate require but a drop of the alkaline solution to redden the indicator.

Soluble salts are isolated by boiling 5–10 grms. of the sample with 100 c.c. of water. Filter and wash. The sulphates are often determined by the barium chloride process (page 618). The barium sulphate may be expressed either in terms of SO_3, or, as is sometimes done, as $ZnSO_4$.

Sulphur dioxide or sulphites are sometimes found in the quick process white leads. Mix 2 grms. of the dried sample with 100 c.c. of recently boiled and cold water in a 300-c.c. Erlenmeyer's flask; add 5 c.c. of concentrated sulphuric acid. Thoroughly agitate the mass. In about 15 minutes, titrate the mixture with $\frac{1}{10}$N-iodine solution, using starch as indicator. Continue the titration until the blue colour develops. One gram of iodine represents 0·252 grm. of SO_2.

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[1] A. Lecrenier, *Bull. Soc. Chim. Belg.*, **18**. 404, 1904; J. A. Schœffer, *Journ. Ind. Eng. Chem.*, **4**. 659, 1912.

[2] G. W. Thompson, *Journ. Soc. Chem. Ind.*, **24**. 587, 1905.

§ 152. The Analysis of Red Lead.

Red lead is usually made by roasting "pig lead" until oxidation ceases. The red lead may contain as impurities or adulterants heavy spar, lead sulphate, silica, ferric oxide, copper oxide, etc. It also contains metallic lead, and various lead oxides—PbO, Pb_2O_3, Pb_3O_4. Silica and clay may be derived from the floor of the muffle in which the red lead was roasted. Owing to the difference in the specific gravity of heavy spar and red lead, good mixing is difficult, and an intimate mixture is liable to segregate when travelling in casks. Hence samples drawn from different parts of the same cask may give different results. Care must therefore be exercised in the sampling.

Dissolve, say, 10 grms. of the given sample in dilute nitric acid (sp. gr. 1·40), or in acetic acid. The dissolution is greatly facilitated by the addition of about 2 c.c. of hydrogen peroxide (5 per cent.)[1] just after the addition of the nitric acid. Heat the solution for about an hour on the water bath. Filter and wash with hot water. The insoluble residue may contain clay, silica, and heavy spar—barium sulphate.[2] This is treated as indicated for white lead (page 320). The clear solution is evaporated to dryness with hydrochloric acid in order to make the silica insoluble, and the latter filtered off. The filtrate from the silica is treated with sulphuric acid in the usual manner, in order to precipitate the lead as sulphate. Keep the amount of acid as low as possible—3 c.c. of concentrated sulphuric acid diluted to 100 c.c. per 10 grms. of red lead will suffice. The filtrate from the lead sulphate is treated with hydrogen sulphide to precipitate the arsenic, antimony, copper, etc., as sulphides. Separate the arsenic and antimony from the copper by means of sodium mono-sulphide (page 277); determine the copper colorimetrically (page 355). If no arsenic or antimony be present, determine the copper in the filtrate from the lead. Iron, zinc, and lime can be determined, if present, in the filtrate from the hydrogen sulphide precipitate (page 276).

Metallic Lead.—Red lead and litharge frequently contain free metallic lead diffused throughout the mass in fine granules—maybe up to 3 per cent.[3] To determine the amount, dissolve a known weight of the red lead in dilute acetic acid at 40° in the presence of hydrogen peroxide. Wash the residue with an acetic acid solution of ammonium acetate, and then with water. Dry and weigh the residue. If other impurities be present, the metallic lead can generally be separated by treatment with dilute nitric acid, and either the washed residue dissolved, dried, and weighed, or the lead determined in the nitric acid solution in the usual manner.

Lead Monoxide.—The presence of lead monoxide, due to imperfect oxidation, is common. Digest the dried sample with a neutral saturated solution of lead acetate in which lead monoxide dissolves. Filter off the insoluble red lead on a weighed Gooch's crucible. Wash, and dry at 100° to constant weight.[1]

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[1] Hydrogen peroxide of commerce sometimes contains sulphuric acid, and in consequence may precipitate lead sulphate. Merck's "perhydrol"—30 per cent. hydrogen peroxide—is satisfactory. Cane sugar, oxalic acid (R. Fresenius, *Anleitung zur quantitativen Analyse*, Braunschweig, **2.** 484, 1903), lactic acid (A. Partheil, *Chem. Ztg.*, **31.** 941, 1907), methyl alcohol, glycerol, formaldehyde, phenylhydrazine, and hydroxylamine hydrochloride have also been suggested (E. Pieszezek, *Pharm. Ztg.*, **52.** 922, 1908 ; F. P. Dunnington, *Zeit. anal. Chem.*, **28.** 338, 1889 ; L. Opificus, *ib.*, **28.** 345, 1889 ; H. Schlossberg, *ib.*, **41.** 740, 1902), but the hydrogen peroxide will be difficult to beat.

[2] Barium sulphate is not a common impurity of normal red lead, since it makes the lead incline to an orange tint. The heavy spar in "tinted red leads" may vary from 10 to 70 per cent. Highly adulterated red lead has been stained with aniline dyes to a good standard colour (M. Frehse, *Ann. Chim. Anal. App.*, **11.** 176, 1906). The dye can be detected by the tint acquired by digesting the red lead in a suitable solvent. Shake 20 c.c. of 95 per cent. alcohol with 2 grms. of the sample, heat to boiling, and let settle. Pour off the alcohol and boil with 20 c.c. of water ; let settle, and proceed in a similar way with ammonium hydroxide. If any of these three solvents have been coloured, the red lead is probably coloured with an organic dye.

[3] G. C. Wittstein, *Dingler's Journ.*, **194.** 84, 1869 ; *Chem. News*, **20.** 249, 1869.

Lead Peroxide.—Digest, say, one gram of dry red lead in a porcelain dish with 20–30 c.c. of dilute nitric acid (1 : 5) on a water bath for a few minutes,[2] when insoluble lead dioxide[3] and soluble lead nitrate are formed. The former may be filtered off, washed, dried at 110°, and weighed. For volumetric determination, add 50 c.c. of $\frac{1}{5}$N-oxalic acid and heat to boiling.[4] Titrate the excess of oxalic acid in the hot solution without filtering by means of a $\frac{1}{5}$N-potassium permanganate solution. If 31 c.c. of permanganate are used, the $50 - 39 = 11$ c.c. of $\frac{1}{5}$N-oxalic acid are used for the reduction of the gram of red lead. From the equation

$$PbO_2 + H_2C_2O_4 = PbO + H_2O + 2CO_2$$

it follows that 1000 c.c. of the $\frac{1}{5}$N-oxalic acid represents 23·9 grms. of PbO_2, or 1 c.c. represents 0·0239 grm. of PbO_2. Hence 11 c.c. of oxalic acid correspond with $11 \times 0·0239 = 0·2629$ grm. PbO_2. Hence, one gram red lead has 0·2629 grm. PbO_2, or 26·29 per cent. PbO_2. The lead monoxide may be determined by calculating the PbO_2 to Pb_3O_4 and subtracting this from the total lead.[5]

In the gravimetric determination of lead peroxide, the sample is digested with warm dilute nitric acid (1 : 5) and allowed to stand in a cool place for 24 hours. Filter through a Gooch's crucible, wash with hot water, dry 6 hours, between 105° and 110°, and weigh as PbO_2. Calculate the corresponding amount of Pb_3O_4 by multiplication with 2·866. The difference between this weight and the weight of the original sample represents litharge. This method is quite unreliable, because lead sesquioxide—Pb_2O_3—dissolves in the nitric acid and is in consequence reported as litharge. The PbO_2 of red lead containing sodium nitrite is attacked by nitric acid more than if the nitrite were absent.

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[1] Lead sesquioxide—Pb_2O_3—is scarcely attacked by the lead acetate—E. E. Dunlap, *Journ. Amer. Chem. Soc.*, **30**. 611, 1908; L. Opificius, *Chem. Ztg.*, **12**. 477, 1898. D. Woodman (*Journ. Amer. Chem. Soc.*, **19**. 339, 1897), using this process, found a variation of 41–92 per cent. in the amount of red lead, and from 8–59 per cent. of lead monoxide, in commercial red leads on the American market. J. Lowe (*Dingler's Journ.*, **271**. 472, 1889) recommends lead nitrate.

[2] F. Lux, *Zeit. anal. Chem.*, **19**. 153, 1880; E. Rupp, *ib.*, **42**. 732, 1903; Schlossberg, *ib.*, **41**. 735, 1902; P. Beek, *ib.*, **47**. 465, 1908; H. Fleck, *Ber.*, **20**. 855, 1881; W. P. Joshua, *Analytische Beiträge zur Bestimmung von Bleisuporoxyd neben Blei uns Bleioxyd*, Zürich, 1906; A. Chevala and H. Colle, *Gazz. Chim. Ital.*, **41**. ii. 551, 1911; *Zeit. anal. Chem.*, **50**. 209, 1911; J. F. Saeher, *Chem. Ztg.*, **35**. 731, 1911.

[3] It is simply a *façon de parler* to say "the PbO_2 content of red lead," since this statement does not imply the existence of PbO_2 in red lead. Red lead is probably not a mixture of PbO_2 and 2PbO. See J. W. Mellor, *Modern Inorganic Chemistry*, London, 795, 1912.

[4] Impurities like sand, barium sulphate, lead sulphate, remain undissolved.

[5] G. Topf (*Zeit. anal. Chem.*, **26**. 296, 1887; W. Diehl, *Dingler's Journ.*, **246**. 196, 1882) heats the red lead with hydrochloric acid and marble, and passes the chlorine evolved into a standard solution of potassium iodide (5 grms. neutral KI, free from iodates) in 100 c.c. of water contained in each of a couple of Péligot's tubes, and estimates the liberated iodine in the regular way, p. 300. V. Farsoc, *Zeit. anal. Chem.*, **46**. 308, 1907. After the action, the iodine solution is titrated with $\frac{1}{10}$N-sodium arsenate. In a sample weighing 0·3624 grm., 10 c.c. of the $\frac{1}{10}$N-sodium arsenate solution were needed. Hence, the red lead contained 32·9 per cent. of PbO_2. C. Marchese (*Gazz. Chim. Ital.*, **37**. ii. 289, 1907) has examined several methods of estimating lead peroxide in red lead—H. Forestier's method (*Zeit. angew. Chem.*, **11**. 176, 1898; *Annal. Lab. Chim. R. Gabelle*, **5**. ii. 486, 1906), in which the red lead is heated for half an hour in a water bath with 10 c.c. of 10 per cent. acetic acid solution, and 20 c.c. of water. The insoluble residue after washing represents "lead peroxide and other insoluble matter." E. Szterkher's method (*Ann. Chim. Anal. App.*, **7**. 214, 1902) depends on the insolubility of lead peroxide in dilute nitric acid – 2 c.c. of acid (sp. gr. 1·18) and 30 c.c. of water—free from nitrous acid. Forestier's method requires a longer heating or stronger acid than is prescribed by its author. Topf's and Szterkher's methods are considered best. A Partheil (*Ver. Ges. deut. Naturforsch. Aertze*, 159, 1907) prefers Topf's process.

§ 153. The Analysis of Lead Chromates.

The chrome yellows and chrome reds are lead chromates or basic lead chromates with more or less lead sulphate, white lead, lead oxide, calcium carbonate, calcium sulphate, zinc oxide, ferric oxide, etc., along with soluble salts due to imperfect washing—potassium sulphate, potassium bichromate, potassium permanganate, etc. A chrome yellow may be considered adulterated if it contains anything besides insoluble lead chromates and lead compounds. The scheme of analysis depends upon the information desired.[1]

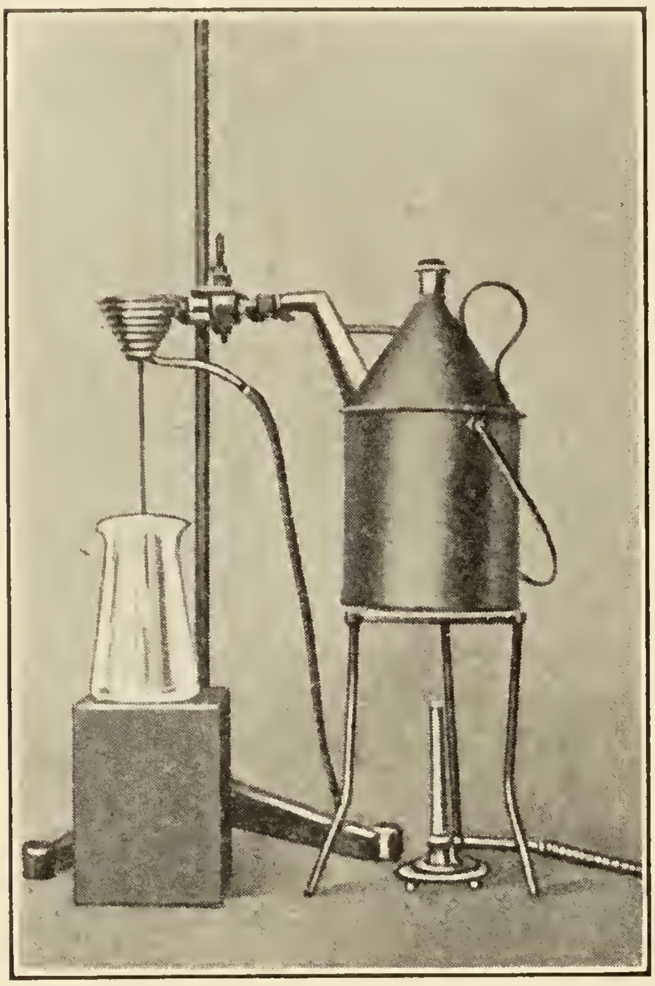

Fig. 130.—Hot funnel.

Insoluble Matter.—Digest 1 grm. of the dry powder (100's lawn) in boiling concentrated hydrochloric acid, adding half a dozen drops of alcohol to the boiling liquid one at a time. This accelerates the dissolution of the lead chromates. Lead chloride—$PbCl_2$—and chromic chloride—$CrCl_3$—are formed. Evaporate the solution to dryness. Add a few drops of hydrochloric acid and 100 c.c. of hot water. Filter the hot solution (a hot-water funnel,[2] fig. 130, is here useful). Wash the residue with hot water,[3] ignite, and weigh. The result is sometimes reported as "insoluble matter"; it contains barium sulphate, silica, etc. The silica can be volatilised by treatment with hydrofluoric acid and sulphuric acid (page 169). The residue is then reported as "barium sulphate," and the loss in weight by the hydrofluoric acid treatment is reported as "silica."[4]

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[1] E. F. Scherubel and E. S. Wood, *Journ. Ind. Eng. Chem.*, **2**. 482, 1910; P. H. Walker, *Bull. U.S. Dept. Agric. Chem.*, **109**. 29, 1910; M. Lachaud and C. Lapierre, *Bull. Soc. Chim.*, (3), **6**. 335, 1891; *Compt. Rend.*, **110**. 1035, 1890.

[2] Hot Funnel.—There are numerous types of hot funnel very useful for filtering hot solutions which have a tendency to crystallise on cooling. In filtering saturated salt solutions liable to crystallise, it is best to use funnels with the stem cut off, *e.g.*, Gattermann's funnel. A good temporary hot-water jacket can be made by wrapping a piece of flexible copper, lead, or "compo" gas piping spirally two or three times round the funnel and blowing steam through the spiral by connecting the pipe with a tin can containing boiling water, fig. 130 (A. Horvath, *Liebig's Ann.*, **171**. 135, 1874; O. von Liebreich, *Chem. Ztg. Repert.*, **11**. 153, 1887; *Zeit. anal. Chem.*, **27**. 387, 1888; **24**. 582, 1885; V. Brudny, *Zeit. Mikros.*, **26**. 418, 1910). Another simple form is a plain sheet zinc or copper bath with a sheet zinc or copper funnel soldered into the bath, so that the glass funnel fits into the metal funnel, with the stem of the glass funnel below the bath. If necessary, the bath can be fitted with a condenser or with a constant level attachment. In Paul's steam-heated funnel (T. Paul, *Ber.*, **25**. 2208, 1886) the steam is blown through a copper tube bent in a spiral form to fit the funnel. The condensed steam returns to the boiler. A simple method of heating by an electric current is also available.

[3] If lead sulphate be present, it must now be washed out by digesting the precipitate with sodium thiosulphate, or ammonium acetate, or ammonium chloride, before ignition, and precipitated from the solution by treatment with hydrogen sulphide (page 276). If the residue be coloured, repeat the digestion with a few drops of hydrochloric acid. Some basic lead chromates may be present, which dissolve very slowly in acids; in that case, the addition of alcohol or hydrogen peroxide is advisable to hasten the process of dissolution.

[4] There are objections to this practice. The alumina of clay, if clay be present, would thus be reported as barium sulphate. For a more exact method of treating the insoluble, see white lead, page 320.

Calcium Sulphate.—Add a hot solution of barium chloride to the boiling filtrate, and determine the sulphates in the soluble portion as barium sulphate (page 322). Calculate the corresponding amount of calcium sulphate by multiplying the weight of the barium sulphate by 0·5837.

Zinc Oxide and Calcium Carbonate.—Digest a gram of the sample with concentrated acetic acid, boil, dilute to 100 c.c., filter, and wash with dilute acetic acid. The zinc oxide, the calcium salts, and some lead oxide pass into solution. Precipitate the lead and zinc by means of hydrogen sulphide, filter, and wash, as described on page 319. Add ammonia to the filtrate until the solution is alkaline; precipitate the lime as calcium oxalate, and proceed as described on page 213. The weight of the calcium oxide so obtained, multiplied by 1·7844, represents the corresponding amount of calcium carbonate. The weight of the calcium sulphate obtained in the preceding determination, multiplied by 0·7351, gives the equivalent amount of calcium carbonate. The difference in the two results represents the amount of calcium carbonate in the given sample.

The mixed lead and zinc sulphides are treated as described on page 320, but the lead sulphate is rejected. The zinc is weighed as phosphate, page 366, and reported as zinc oxide.

Ferric Oxide and Lead Chromate.—Boil 1 grm. of the powdered sample with about 10 grms. of potassium hydroxide and 100 c.c. of water, filter, and wash with hot water. The alkaline filtrate containing the lead chromate in solution is acidulated with acetic acid, and insoluble lead chromate will be precipitated. This is collected on a weighed Gooch's crucible, washed with water, dried at 110°, and weighed as lead chromate—$PbCrO_4$.

The filter paper contains the ferric oxide, barium sulphate, silica, and lead oxide. Ignite the mixture slowly in a porcelain crucible so as to prevent the mass sticking to the sides of the crucible. Digest the residue with 5 c.c. of hot concentrated hydrochloric acid, and transfer the mixture to a beaker with 50 c.c. of water. Filter off the insoluble silica and barium sulphate. Nearly neutralise the filtrate with ammonia and precipitate the lead as lead sulphide. Wash and reject the precipitate. The filtrate is boiled to expel the hydrogen sulphide, and treated with a few drops of nitric acid to oxidise the iron. The iron is precipitated with ammonia, washed, ignited, and weighed as ferric oxide (page 182).

Total Lead Oxide.—One gram of the sample is digested with concentrated hydrochloric acid, evaporated to dryness, and the mixture treated with a few drops of hydrochloric acid and about 100 c.c. of hot water. Boil the solution until it has a clear green colour. Add 5 to 10 grms. of sodium acetate to replace the free hydrochloric acid by acetic acid.[1] Add 5 c.c. of acetic acid and a gram of potassium chromate. Stir the solution vigorously. The lead chromate is precipitated. Filter through a weighed Gooch's crucible, wash the precipitate with water, dry at 110°, and weigh as lead chromate—$PbCrO_4$.[2] The difference in the weight of the lead chromate so determined and that previously obtained is multiplied by 0·6903, and the result reported as lead monoxide—PbO.

White Lead.—If white lead be present, determine the amount of carbon dioxide in the given sample (page 552 or 553), and deduct the carbon dioxide corresponding with the calcium carbonate previously determined. The result, multiplied by 17·62, gives the corresponding amount of white lead—$Pb(OH)_2 . 2PbCO_3$. The amount of white lead is multiplied by 0·2877 to get the corresponding amount of lead oxide—PbO. This is deducted from the lead oxide previously obtained.

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[1] If iron be present, the solution turns reddish-brown.

[2] The separation of lead as chromate is sometimes advantageous under conditions where the sulphate, sulphite, or molybdate separations would be less convenient. This, for instance, is the case in separating small quantities of lead from copper and zinc in acetic acid solutions, and in separating lead from silver in ammoniacal solutions. If bismuth be present, some bismuth chromate will be precipitated with the lead chromate, and the two must be separated by other methods—W. Diehl, *Chem. Ind.*, 6. 157, 1883.

Soluble Salts.—The soluble salts—acetates, bichromates, sulphates, nitrates, etc.—present are generally derived from imperfect washing in the manufacture of the chromate. The soluble salts are determined by weighing, say, 5 grms. of the dry (109°) impalpable powder on to an asbestos Gooch's crucible (dried at 109°), and washing six times with 25 c.c. of cold water. Dry the contents of the crucible at 109° and weigh. The loss in weight represents the soluble salts removed by the water. The washings may be examined, if desired, and the salts just named specially determined qualitatively, or quantitatively.[1]

Results.—Scherubel and Wood's test analysis on a known mixture gave the following percentage results:—

	SiO_2.	$BaSO_4$.	Fe_2O_3.	$CaSO_4$.	ZnO.	$CaCO_3$.	$PbCrO_4$.	PbO.
Used . .	4·76	4·76	4·76	4·76	9·52	4·76	57·14	9·54
Found . .	4·52	4·70	4·88	4·90	4·54	4·64	57·04	9·68

These results must be considered satisfactory for technical work.

Naples Yellow.—In evaluating this substance, lead and antimony are to be separated. Determine the antimony volumetrically in an aliquot portion of the solution: the lead may be determined by precipitation as sulphide by hydrogen sulphide in an alkaline solution, hot, if necessary, to keep the lead chloride in solution.[2]

§ 154. The Determination of Silver in Lead Compounds by the Turbidity Method.

Silver in small quantities is best determined by cupellation. The amount present in red lead, white lead, etc., is usually too small to be determined satisfactorily by other gravimetric[3] or volumetric processes. Blunt[4] determines the silver by the following turbidity process:—Dissolve 10 grms. of, say, red lead in 50 c.c. of dilute nitric acid (sp. gr. 1·42, 1 vol.; water 4 vols.) quite free from chlorides. Dilute to 120 c.c.; filter; wash the residue with a little distilled water; make the solution up to 200 c.c.; pipette 100 c.c. into the left test glass of the colorimeter. The other 100 c.c. is treated with a drop of concentrated hydrochloric acid and stirred. The lead chloride passes into solution and the silver chloride produces a white turbidity. Let all stand an hour; and filter the solution into the right test glass of the colorimeter through a small 5·5-cm. filter paper. Wash with distilled water. Add a standard solution of silver nitrate[5] drop by drop with constant stirring until the turbidity in both vessels appears the same. The volume of the silver nitrate solution used represents the amount of silver in the given solution. See page 654.

§ 155. The Determination of Silver and Gold by Cupellation.

This process is very old, and an enormous number of determinations of gold and silver by this process are made daily in assay offices in different parts of the world. A known weight of the lead compound is reduced to the metal. The metal is then heated in a vessel, called a *cupel*, made of bone ash, or some other suitable material, whereby the lead is oxidised and absorbed by the cupel; the silver remains behind as a small bead. The silver will be alloyed with gold, if gold be present.

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[1] In this case probably more powder will be needed.

[2] The lead may also be precipitated as oxalate, and the lead oxalate determined by titration with potassium permanganate, as indicated for lime (page 215).

[3] Precipitation as silver chloride or iodide.

[4] T. P. Blunt, *Chem. News*, **32**. 3, 1875; J. Krutwig, *Ber.*, **15**. 307, 1264, 1882.

[5] Silver Nitrate Solution.—Dissolve 1·575 grms. silver nitrate in water and make the solution up to a litre. 1 c.c. represents 0·001 grm. of silver—Ag.

Roasting and Fusion.—The object of the fusion is to collect the silver in a button of metallic lead—silver alloy. Intimately mix 100–120 grms. of dry litharge, red lead or white lead, with the flux—sodium bicarbonate 60 grms., argol 2 grms.—on a sheet of glazed paper. The mixture is transferred to a fire-clay crucible so as to fill the crucible not more than three-quarters full,[1] and the whole contents covered with a layer of finely powdered dry borax glass. The lid is placed on the crucible and the whole heated gradually to prevent breaking the crucible or prevent the charge from blowing. When the contents of the crucible have ceased bubbling and all is in a state of quiet fusion, the crucible is removed from the fire and gently tapped, sides and bottom, in order to assist the molten metal inside to collect on the bottom of the crucible. The molten contents of the crucible are usually poured into conical iron moulds; or the crucible may be allowed to cool, and then broken. The slag is separated from the lead button by hammering the button on an anvil into a cube with its corners flattened.[2] The button should weigh about 20 grms. If it weighs more, use less argol; if less, more argol.

Cupellation.—The object of the cupellation is to remove the "base" metals by oxidation and absorption in the cupel. The "noble" metals—gold and silver—remain on the cupel bottom after the operation in the form of a small bead. Place three or four empty cupels[3] in a red-hot muffle.[4] In about 10 minutes the button of lead is placed by means of the "cupel tongs" in the centre of a hot cupel free from cracks. Close the door of the muffle. The lead melts (326°); a black scum develops on its surface. This disappears in a few minutes (about 675°), and the molten lead has a bright silvery appearance. The door of the muffle should be opened, but not wide enough to allow cold air to impinge directly on the muffle. Oxidation now sets in vigorously. The flakes of oxide which form on the surface of the button "slide" down the convex surface of the button and are absorbed by the cupel. The temperature of the cupel should not exceed 750°—a temperature below the melting point of litharge (about 900°).

The most common mistake at this stage is too high a temperature. If the temperature of the muffle is right, "feathers" of litharge appear on the side of the cupel near the doors and on the upper rim of the cupel. If the temperature is too low, feathers form low down in the cupel. If the muffle be not hot enough, put a lump of charcoal in front of the muffle. This will raise the temperature a little.

Sometimes the action stops during cupellation and the button solidifies. This is called "freezing." This arises when the lead has been oxidising more rapidly than the lead oxide has been absorbed by the cupel. In that case add more lead to the cupel. If "freezing" be due to the low temperature of the muffle, the temperature of the latter must be raised a little. The result of a cupellation with a button which has frozen is to be regarded with suspicion.

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[1] Say, a Battersea round, approximately size E.

[2] If portions of lead or pasty-looking masses adhere to the sides of the crucible, the fusion is defective, and another fusion must be made.

[3] Shallow cups of bone ash or other suitable material. The success of the work is largely dependent on the quality of the cupel. If many cupels are required, they can be made with good bone ash in "cupel moulds"; if but few determinations are to be made, old and dry cupels of good quality can be purchased from the dealers. A good cupel will absorb its own weight of lead oxide. The cupel should be nearly twice as heavy as the lead button.

[4] That is, varying from "red" to "bright red." Not "dull red," nor "white."

Traces of foreign metals—copper, antimony, iron, zinc, etc.—are partly absorbed by the cupel, and partly volatilised as oxides. As the absorption of lead continues, the button becomes more and more spherical. At this stage the temperature of the muffle should be raised, or the cupel pushed into a hotter part of the muffle. When the last of the lead has gone, the button appears to revolve axially in the cupel, and it also seems to be covered with an iridescent film. The colours disappear; the bead becomes dull and acquires a silvery tinge. If the temperature of the muffle be below the melting point of the button (962° for silver), or if the cupel be withdrawn from the muffle, the bead suddenly becomes very bright—"flashing." Close the doors of the muffle for one or two minutes so as to remove the last traces of lead.

The cupel may then be covered by placing a hot empty cupel over the one containing the bead, and the cupels removed from the muffle. The object, of course, is to ensure slow cooling in order to prevent "sprouting" caused by the evolution of occluded oxygen by the silver bead. If the bead should sprout, start again. When cold, the bead is removed with a pair of forceps. If the bead be excessively small, merely touching it with a wet pin and lifting it on to a watch-glass will suffice. Dry the bead by warming, and weigh.[1] The bead should be examined with a lens before weighing to make sure that no particles of bone ash adhere to the bead. If the bead is so contaminated, hold it in the "bead forceps," and brush it clean with a hard brush—"button brush."

The bead contains both gold and silver. If the bead is white, it contains more than half its weight of silver; if yellow or reddish-yellow, it has about three-quarters of its weight gold. Intermediate tints represent different proportions of gold and silver. For the determination of the amount of gold in the bead, see page 432. In the case of red and white leads, if the silver be determined at all, it will usually suffice to report the weight of the bead as "silver."

§ 156. The Analysis of Galena.

Native galena—PbS—may be accompanied by products of the decomposition of lead sulphide—anglesite and cerusite—quartz, silicates, blende, calcite, fluorspar, heavy spar, and pyrites. Certain varieties also contain arsenic and antimony; and argentiferous galena may contain up to 1·0 per cent. of silver.

Decomposition of the Galena.—Moisten, say, half a gram of the finely divided sample in a 250-c.c. basin with dilute nitric acid; and, after the cold mixture has stood for a few minutes, digest on the water bath with 15 c.c. of concentrated nitric acid. The basin is covered by a clock-glass during the reaction to prevent loss by spurting. When the violence of the action is over, evaporate the mixture to dryness on the water bath.[2] Add 10 c.c. more of concentrated nitric acid, some water, and 10–15 drops of bromine. Heat the mixture with frequent stirring on the water bath, so as to complete the oxidation of the sulphide. To decompose the bromates, add more nitric acid, and evaporate to dryness. Repeat this operation in all three times. Boil the dry residue with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid so as to dissolve the lead sulphate. Filter off[1] the residual gangue; wash well with boiling water. If desired, the residue may be ignited, weighed, and reported as "insoluble gangue." This may contain the quartz, insoluble silicates, some silver chloride, and the greater part of the barium sulphate.[2]

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[1] If the bead of silver be too small to weigh, its volume can be measured with the microscope. Suppose the bead has a diameter 0·18 mm. For the method of measuring under the microscope, see the next volume of this work. The measurement is supposed to be the average of measurements in two or three different directions. The volume of the bead is $0{\cdot}5236 \times (0{\cdot}18)^3$ cub. mm. If the specific gravity of the silver be 10·5, the bead of silver will weigh $10{\cdot}5 \times 0{\cdot}5236 \times (0{\cdot}18)^3 =$ 0·032 mgrm. or 0·000032 grm. V. Goldschmidt, *Zeit. anal. Chem.*, **17**. 142, 1878; **16**. 434, 1877; C. F. Föhr, *ib.*, **22**. 195, 1883; *Chem. News*, **50**. 114, 1884; G. Tate, *ib.*, **61**. 43, 54, 1890; G. A. Gozdorf, *ib.*, **54**. 231, 1886; D. Forbes, *ib.*, **15**. 231, 1867; G. A. Goyder, *ib.*, **70**. 194, 203, 1894; J. W. Richards, *Journ. Amer. Chem. Soc.*, **23**. 203, 1901; J. S. Curtis, *Berg. Hütt. Ztg.*, **47**. 3, 1888; M. Guerreau, *Bull. Soc. Chim.* (3), **27**. 1902; *Chem. News*, **86**. 194, 1902.

[2] A little hydrochloric acid generally aids the dissolution of the galena by dissolving the film of lead nitrate, which is almost insoluble in the strong acid, and thus protects the galena from further attack.

Transformation of the Decomposition Products into Sulphates.—Add 10 c.c. of dilute sulphuric acid (1 : 1) to the filtrate (or an aliquot portion of the filtrate) from the insoluble gangue, and evaporate the mixture until copious white fumes of sulphuric acid appear. The evaporation should be carried nearly to dryness in order to ensure complete conversion of the lead salts into sulphates; to prevent too large an excess of acid; and to drive off the nitric and hydrochloric acids. Let the mixture cool.

Separation of the Lead Sulphate.—Gradually add 100 c.c. of cold water, and boil the mixture so as to dissolve the ferric sulphate, etc. The lead sulphate remains behind, insoluble. Decant the clear solution through a filter paper, and wash by decantation with dilute sulphuric acid, as indicated on page 317. If the lead sulphate is to be determined gravimetrically, transfer it[3] to a Gooch's crucible or filter paper, as indicated on page 318; if the lead is to be determined volumetrically,[4] keep as much solid in the beaker as possible. Wash the paper with alcohol to remove sulphuric acid. Dissolve the precipitate on the paper by pouring a hot concentrated solution of ammonium acetate, slightly acidulated with acetic acid, through the filter paper into the beaker containing the remainder of the lead sulphate. The amount of lead in the ammonium acetate solution can then be determined by the molybdate volumetric process (page 333). Bad results by this process can often be traced to an imperfect dissolution of the lead sulphate on the filter paper, etc.

Determination of Other Constituents.—Copper, antimony, and arsenic can be precipitated as sulphides from the filtrate, and the copper separated from the antimony and arsenic, as indicated on page 277. The copper can be determined as indicated, page 351; the antimony and arsenic determined as indicated, page 304. The filtrate is boiled to drive off the hydrogen sulphide, oxidised with a few drops of hydrogen peroxide, and heated to boiling with an excess of ammonium chloride and a slight excess of ammonia. The precipitate is treated as indicated on page 182. Zinc, if present, will be found in the filtrate, and determined as indicated on page 366. The sulphur can be determined by oxidising the powdered sample with nitric acid and bromine, and finally weighed as barium sulphate (page 618).

Other Methods of "Opening" Galena.—Other methods of decomposition are sometimes useful alternatives. Galena, for example, can be reduced to "metal"[5] by fusing a mixture of, say, 25 grms. with 75 grms. of potassium cyanide, and covered with a layer of 12 grms. of powdered anhydrous borax. Cover the crucible with a lid, and heat the mixture to redness for about 5 minutes (page 269). The metallic button is washed free from cyanide, dissolved in dilute nitric acid (1 : 5), and treated for lead by the sulphuric acid process (page 317).

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[1] If lead only is to be determined by a volumetric process, this filtration may be omitted.

[2] The difference in weight after treatment with hydrofluoric acid will give the silica. Fusion with sodium carbonate and extraction with water will give an insoluble residue of the carbonates. These can be dissolved in nitric acid. the silver precipitated with hydrochloric acid, and the barium with sulphuric acid (pages 652 and 618). The total silver may be determined by cupellation.

[3] Of course, previously freed from "insoluble gangue."

[4] If the amount of lead is alone to be determined volumetrically, there is no need to filter off the "insoluble gangue."

[5] A. W. Warwick, *Chem. News*, 63. 30, 145, 1891; F. Jean, *Bull. Soc. Chim.* (3), 9. 253, 1893.

The sodium peroxide fusion (page 266) is often most convenient for the determination of sulphur; and the process indicated by footnote, page 326, enables a determination of the lead to be made very quickly.[1]

§ 157. The "Government Test" for the Solubility of Lead Frits.

The directions given in the *Home Office Circular*[2] for this test are as follows:—

> "No glaze into the composition of which the fritted lead enters shall be regarded as satisfying the requirement as to insolubility which yields to a dilute solution of hydrochloric acid more than 2 per cent. of its dry weight of a soluble lead compound calculated as lead monoxide, when determined in the following manner:—A weighed quantity of dried material is to be continuously shaken for one hour, at the common room temperature, with 1000 times its weight of an aqueous solution of hydrochloric acid containing 0·25 per cent. of HCl. This solution is thereafter to be allowed to stand for one hour and to be passed through a filter. The lead salt contained in an aliquot portion of the filtrate is then to be precipitated as lead sulphide and weighed as lead sulphate."

The directions here are incomplete. It is difficult, indeed impossible, to filter some glazes satisfactorily through filter paper; and if some silica gets into solution, it may, later on, be precipitated with the lead sulphide. Hence, dry the glaze at 100°.[3] Transfer, say, 0·5 grm. of the powder into a 500-c.c. Stohmann's shaking bottle closed with a rubber stopper, and fill the bottle up to the mark on the neck[4] with 0·25 per cent. hydrochloric acid. Shake the mixture for an hour in, say, Wagner's shaker, fig. 131. Let the bottles stand for one hour. Filter off a convenient quantity, say, 425 c.c. of the clear solution.[5] Evaporate to dryness on a water bath. Take up the residue with dilute hydrochloric acid, so that the solution is but slightly acid (page 276). Filter and wash the silica. Add 1 c.c. of a saturated solution of mercuric chloride (page 319). The mercury may be ignored, because it is volatilised later on. Precipitate the lead as sulphide by means of hydrogen sulphide. Let the gas bubble slowly through the cold solution for about half an hour. Let the precipitate settle about an hour. Filter and wash with cold "H_2S" water. The precipitate is supposed to be lead sulphide.[1] Incinerate the precipitate in a porcelain crucible at a low temperature[2] in order to burn off the filter paper. Brush the residue into a 250-c.c. beaker. Wash the crucible with dilute nitric acid and proceed as indicated for lead sulphate (page 317).

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[1] R. Benedict (*Chem. Ztg.*, **16**. 43, 1896) decomposes galena by digestion with hydriodic acid (sp. gr. 1·7). Subsequent digestion with nitric acid transforms the lead iodide into nitrate, and the lead is then precipitated as sulphate. According to F. H. Storer (*Chem. News*, **21**. 137, 1870; A. Mascazzini, *Zeit. anal. Chem.*, **10**. 491, 1871; F. Stolba, *Journ. prakt. Chem.* (1), **101**. 150, 1867; F. Mohr, *ib.*, **12**. 142, 1873), galena is decomposed rapidly and completely—by dilute hydrochloric acid (1 : 4) in contact with metallic zinc. Besides galena, metallic lead may be precipitated quickly and completely from the sulphate, nitrate, chromate, oxide, carbonate, and chloride. The clear liquid decanted from the residue shows no trace of lead with hydrogen sulphide. C. Boucher (*Bull. Soc. Chim.* (3), **29**. 933, 1904; *Chem. News*, **89**. 56, 1904) attacks pyrites and galena by heating the powdered mineral intimately mixed with 4 to 5 times its weight of a mixture of 3 parts of sodium persulphate with 1 of ammonium nitrate in a dish or flask on a sand bath. For other methods of analysing galena, see J. A. Müller, *Bull. Soc. Chim.* (3), **31**. 1303, 1904; *Chem. News*, **92**. 15, 1905; P. Jannasch and H. Kammerer, *ib.*, **72**. 78, 1895; *Ber.*, **28**. 1409, 1895; J. K. Meade, *Journ. Amer. Chem. Soc.*, **19**. 374, 1897: *Chem. Eng.*, **11**. 49, 1910; *Chem. News*, **101**. 137, 1910; W. Stahl, *Berg. Hütt. Ztg.*, **48**. 237, 1889.

[2] K. E. Digby, *Home Office Circular*, Dec. 14, 1889.

[3] If a slop glaze be supplied, it must be thoroughly agitated and a portion evaporated to dryness, and the dry powder thoroughly mixed. Special attention is here needed, because the glaze is not usually homogeneous after it has been dried in a basin on the water bath.

[4] 500 grms., or 499·4 c.c. of 0·25 per cent. acid at 15°. The method in the text is sufficiently exact.

[5] Reject the first 10 c.c. which pass through the paper.

The weight of the lead sulphate, multiplied by 0·7359, gives the corresponding amount of lead monoxide—PbO—in the 425 c.c. of solution. Hence, by proportion, calculate the amount in the 500 c.c., that is, in 0·5 grm. of the glaze. The result multiplied by 200 gives the so-called "percentage solubility of the lead frit," or "per cent. of soluble lead" in terms of lead monoxide. The differences obtained in duplicate determinations with quantities of "soluble lead" up to 10 per cent. run to about ± 0·1 per cent.; for larger quantities—20 to 40 per cent. "soluble lead"—differences in the duplicates run about ± 0·2 per cent.

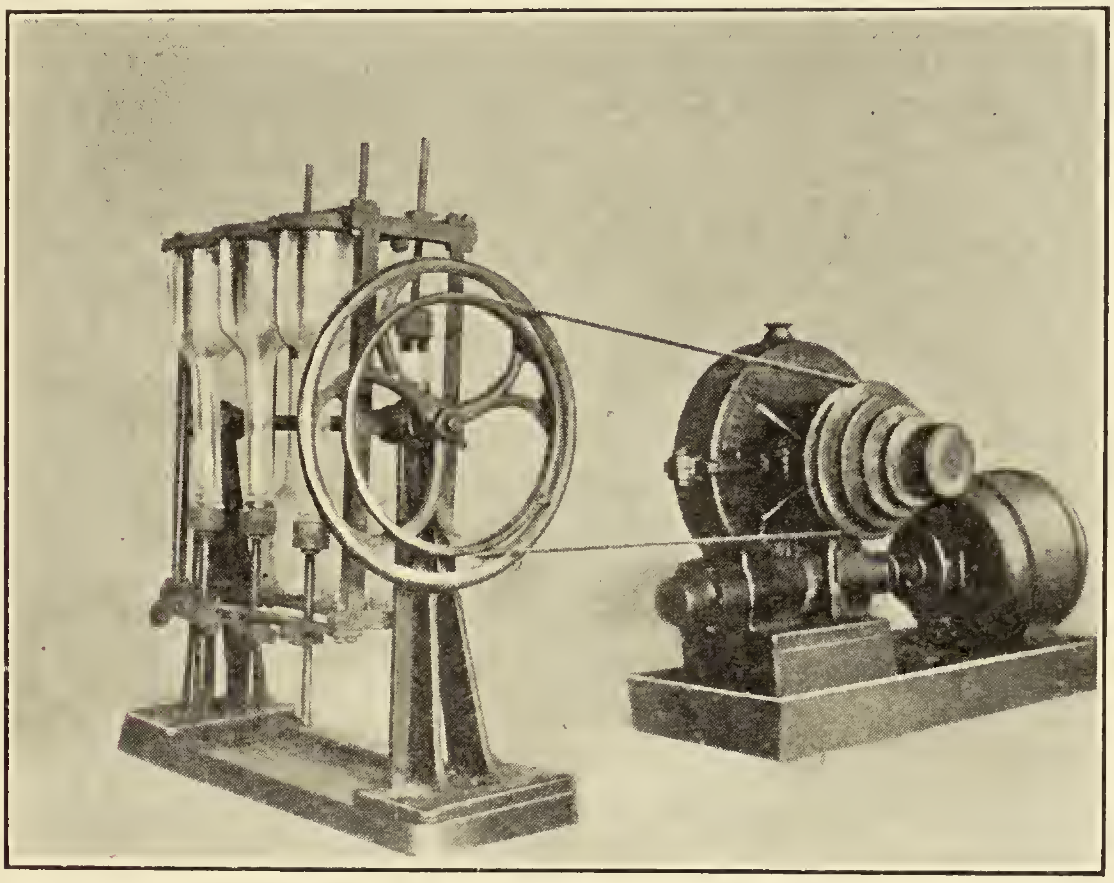

Fig. 131.—Shaking apparatus.

§ 158. The Gravimetric Determination of Lead as Molybdate.

Lead can also be advantageously determined as molybdate and as chromate. The advantage of the molybdate precipitation is that the precipitate may be ignited along with the paper, and no particular harm results from a prolonged ignition at a higher temperature than is required to destroy the paper. The errors in manipulation are also reduced more in calculating the weight of the molybdate to PbO than with the corresponding sulphate or chromate. The reaction has been studied in particular by Chatard[1] and Brearley, and Chatard's description of the disturbing effect of an excess of the precipitating agent has led to the process being viewed with a suspicion which the method may not deserve.

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[1] Many glazes contain a little zinc oxide, and some zinc sulphide might be precipitated from the dilute acid with the lead sulphide. Note, other members of the hydrogen sulphide group might be present, and unless a separation were made, the "PbO solubility" would be too high.

[2] If much lead be present, the filter paper had better be ignited alone (page 317). Instead of following the method described in the text, the lead sulphide and filter paper can be incinerated until the paper is charred to carbon; when nearly cold, carefully add a little fuming nitric acid, a drop at a time, from a pipette. The carbon will be oxidised, and the lead sulphide transformed into sulphate. This method requires a little practice, but it saves a great deal of time and is more exact than the roundabout method described in the text, once the manipulation is mastered.

Suppose that the lead salt be in solution, add a slight excess of ammonia and then acidify the solution with acetic acid. Add about 5 grms. of ammonium chloride, and heat the solution to boiling.[2] An excess of an aqueous solution of ammonium molybdate[3] is then gradually added with constant stirring. Boil the solution two minutes. Let the cream-coloured precipitate gradually settle until cold. Filter through a weighed Gooch's crucible. Wash with hot water containing about 2 per cent. of ammonium acetate in solution. Ignite and weigh as lead molybdate—$PbMoO_4$. Multiply the weight of the lead molybdate so obtained by 0·6077 to get the corresponding weight of lead monoxide—PbO.

The result is not more than 1 per cent. out with the elements which form insoluble molybdates—nickel, zinc, cobalt, magnesium, aluminium—and the effects of these elements, together with calcium,[4] strontium, and barium, if present, can be eliminated by reprecipitation. Arsenates and phosphates should not be present. The slight excess of free molybdic acid which may contaminate the first precipitate is eliminated by reprecipitation.

For reprecipitation, dissolve the precipitate of lead molybdate in hydrochloric acid; heat the solution to boiling; add a sufficient excess of ammonium acetate to neutralise the free hydrochloric acid, and proceed as described above.

The lead may be first precipitated as sulphate. Dissolve the sulphate in a concentrated solution of ammonium acetate, and add an excess of ammonium molybdate, as indicated above. Excellent results can be obtained by this method.

§ 159. Conversion Factors.

In gravimetric analyses it is comparatively rare to find that the constituent to be determined can be weighed directly, as were silica, alumina, ferric oxide, and lime. In most cases the constituent to be determined is separated as an "insoluble" salt—barium sulphate, lead sulphate, silver chloride, magnesium pyrophosphate, etc., and the corresponding amount of baryta, lead oxide, silver, magnesia, etc., determined by multiplying the observed weight by a factor, the so-called conversion factor. The errors of experiment are obviously multiplied at the same time. Any error in the preparation and weighing of the precipitate of, say, lead sulphate—$PbSO_4$—in the determination of the lead oxide will be distributed between the lead oxide and the sulphuric anhydride. In lead sulphate: $PbO : SO_3 = 3 : 1$, very nearly; or, more exactly stated, the conversion factor for transforming the lead sulphate to lead oxide is 0·7359. Hence, a total error of ± 0·8 per cent. in the determination of the lead sulphate corresponds with an error of ± 0·6 in the determination of the lead oxide. If the lead be determined as lead molybdate—$PbMoO_4$—we have very nearly: $PbO : MoO_3 = 3 : 2$; or, more exactly, the conversion factor for transforming the weight of the lead molybdate to lead oxide is 0·6077. Hence, an error of 0·8 per cent. in the determination of the lead molybdate means that there will be an error of 0·5 in the determination of the lead oxide. Consequently, other things being equal, *the smaller the factor the less the influence of errors in the determination upon the final result.* Hence, given two rival analytical processes which are liable to errors of experiment of the same magnitude, and which involve the same amount of manipulation, that process will be chosen which has the least conversion factor. For this reason, among others, silver is better precipitated as bromide than as chloride. The conversion factor in the former case is 0·5744, and in the latter 0·7526. As a matter of fact, in spite of the theoretical advantages of the bromide process, the chloride process is preferred by many because the sources of error and corrections have been well explored for the chloride process, but not for the bromide process.

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[1] T. M. Chatard, *Chem. News*, 24. 175, 1871; *Amer. J. Science* (3), I. 416, 1871; J. F. Sacher, *Chem. Ztg.*, 33. 1257, 1909; see page 414.

[2] The precipitate is difficult to filter in the absence of this or some other coagulating salt.

[3] AMMONIUM MOLYBDATE SOLUTION.—Dissolve 34·34 grms. of ammonium heptamolybdate in water; make the solution faintly acid with acetic acid; and make the solution up to litre ($\frac{1}{6}$E).

[4] Calcium molybdate is very prone to precipitation with the lead molybdate.

§ 160. The Volumetric Determination of Lead—Molybdate Process.

Schindler, in 1888, proposed to determine lead as lead molybdate by means of a standard solution of ammonium molybdate. The titration is made in a hot ammonium acetate solution of lead sulphate slightly acidified with acetic acid.[1] The reaction is symbolised :

$$Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 \rightarrow PbMoO_4 + 2NH_4C_2H_3O_2.$$

According to Kroupa, the presence of arsenic, antimony, bismuth, phosphorus, and zinc does not interfere with the process. Barium and strontium salts lead to low results. These substances appear to act by retarding the dissolution of the lead sulphate. The difficulty is overcome by repeatedly boiling the sulphate with hot ammonium acetate to ensure complete solution. Bannister and M'Namara found that the results are high if calcium salts be present. *E.g.*, with test solutions containing the equivalent of 0·2005 grm. of lead and 0 to 0·2415 grm. of calcium sulphate, the results ranged from 100 to 109 per cent. of lead in place of 100.

About a gram of the lead—say, white lead—is dissolved in acetic acid or in dilute nitric acid ; for the dissolution of red lead, see page 322. The insoluble sulphates are filtered off. The lead is precipitated as sulphate, filtered, and washed, as indicated, page 319. If calcium salts be present, special care must be taken to wash out the calcium sulphate before proceeding further. The precipitate is dissolved in a concentrated solution of ammonium acetate. Acidify the solution with 2–3 c.c. of acetic acid, and heat the solution to boiling. Titrate the hot solution with standard ammonium molybdate[2] from a burette until a drop gives a slight but distinct yellow coloration with a drop of freshly prepared[3] aqueous solution of tannin—spot test. If the solution cools during the titration, it should be heated again to finish the titration.

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[1] C. Schindler, *Zeit. anal. Chem.*, **27**. 137, 1888 ; H. Weber, *ib.*, **42**. 628, 1903 ; I. C. Bull, *ib.*, **41**. 653, 1902 ; *School Min. Quart.*, **23**. 348, 1903 ; *Chem. News*, **87**. 40, 52, 66, 1903 ; H. H. Alexander, *Eng. Min. Journ.*, **55**. 298, 1893 ; J. F. Sacher, *Chem. Ztg.*, **33**. 1257, 1909 ; J. A. Müller, *Bull. Soc. Chim.* (3), **31**. 1303, 1904 ; R. Kroupa, *Berg. Hütt. Ztg.*, **53**. 411, 1894 ; J. F. Sacher, *Chem. Ztg.*, **33**. 1257, 1909 ; C. O. Bannister and W. M'Namara, *Analyst*, **37**. 242, 1912. See *Chem. Eng.*, **16**. 36, 1912.

[2] STANDARD AMMONIUM MOLYBDATE SOLUTION.—Dissolve 8·022 grms. of ammonium molybdate in water and dilute the solution to a litre. If the solution be turbid, add some ammonia before the dilution is completed—1 c.c. will be nearly equivalent to 0·01 grm. PbO. To standardise the solution, dissolve, say, five known amounts of lead sulphate in hot ammonium acetate ; add 2–3 c.c. of acetic acid ; and titrate as indicated in the text. Schindler also uses the converse reaction, titration with standard lead acetate, for the volumetric determination of molybdenum.

[3] TANNIN SOLUTION.—About 0·5 grm. of tannin dissolved in 100 c.c. of water. Ammonium molybdate gives with tannin a coloration varying from blood-red to a pale yellow, according to

Titrating with "Spot-test" Indicators.—It is easy to over-titrate the solution when using "spot-test" indicators, and three methods of titrating to rectify or avoid over-titration may be indicated: (1) Some prefer to use a standard solution of lead nitrate [1] for checking the first titration. Suppose the titration is finished, add 10 c.c. of the standard lead nitrate solution, and continue the titration. 0·1 grm. of lead must be subtracted from the result of the titration.

(2) For the titration it is well to place about half the solution to be titrated in a separate beaker and titrate the other half by adding a cubic centimetre of the ammonium molybdate solution at a time, in order to get a rough idea of the amount needed. Suppose the one portion requires between 15 and 16 c.c. for the titration (no coloration with 15 c.c.; yellowish-brown coloration with 16 c.c.). Add the untitrated portion to the portion just titrated, and 14 c.c. can be safely run from the burette, and the titration finished by small additions from the burette.

(3) In titrating with a spot test, particularly with slow reactions, the testing should be done systematically. Suppose the first stop be made at 29 c.c., the second at 29·2 c.c., the third at 29·4 c.c., and so on. If the brown coloration develops on the sixth spot, it would mean that $29 + (n - 1)0{\cdot}2 = 30{\cdot}0$ c.c. has been added ($n = 6$). But the coloration may develop on the fourth spot *after* it has been passed. It is then easy to determine the burette reading for the fourth spot—namely, $29 + (n - 1)0{\cdot}2 = 29{\cdot}6$ c.c., where $n = 4$.

Lead carbonate may also be precipitated by the addition of ammonium carbonate; the precipitate dissolved in acetic acid; and the solution titrated with potassium ferrocyanide,[2] as indicated under zinc. The results are good.

§ 161. The Electrolytic Process for the Determination of Lead.

Metallic lead can be readily deposited from alkaline electrolytes containing phosphates, alkaline plumbate, double oxalates, double cyanides, etc. But it is so difficult to dry the lead for weighing without oxidation, that it is considered better to take advantage of the fact that lead is deposited from acid solutions in the form of lead dioxide—PbO_2—on the anode, not the cathode. Hence, the dish, with its inner surface matt, is fitted as described on page 256, fig. 118; but the direction of the current is reversed so that the dish is the anode, and the platinum disc the cathode. The details indicated on page 258 are to be followed, with the modifications indicated in the following paragraphs.

The Electrolyte.—Suppose that 1 grm. of lead nitrate be dissolved in 30 c.c. of distilled water. Add 25–35 c.c. of concentrated nitric acid. Dilute the solution to 150–160 c.c.

The Electrolysis.—Electrolyse the solution with a current density of 0·5 to 1·8 amps.,[3] and a voltage of 2·0 to 2·5 volts, at atmospheric temperatures.[4] As

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the concentration of the solutions. The colour is visible with a dilution 1 : 400,000 (Schindler). Lead molybdate gives no coloration. Concentrated solutions of lead acetate give a faint greenish-yellow colour, which cannot be confused with the coloration due to ammonium molybdate. J. L. Danziger uses a solution formed by saturating acetic acid with crystalline stannic chloride and saturating the solution with ammonium thiocyanate. When this is used instead of tannin as indicator, the end of the reaction is indicated by a pink coloration—spot test.

[1] LEAD NITRATE SOLUTION.—16 grms. of lead nitrate per litre corresponds with 0·01 grm. lead per c.c.

[2] M. Yvon, *Journ. Pharm. Chem.* (5), **19**. 18, 1889; A. H. Low, *Journ. Amer. Chem. Soc.*, **15**. 548, 1893.

[3] For an overnight electrolysis (10–12 hours), use a current density of 0·5 amp.

[4] If the operation be conducted at 50°–55°, the time required for the electrolysis is shortened to between 1 and 1½ hours, using a current density of 1·3 to 1·6 amps., and 2·2 to 2·6 volts.

soon as electrical circuit is closed a yellow deposit appears on the anode (dish), which becomes orange, red, and finally dark brown or black. The electrolysis occupies between 2 and 3 hours.[1] If a deposit of metallic lead should appear on the platinum disc (cathode) during the electrolysis, add a little more concentrated nitric acid; or interrupt the current for about half a minute during the middle and towards the end of the electrolysis.

When the electrolysis is complete, the deposit is washed with water, absolute alcohol, and absolute ether in the usual way. If the electrolyte be syphoned off before the current is stopped (fig. 119, page 260), keep the deposit quite covered with liquid all the time the syphon is in action. In other words, pour distilled water into the dish as fast as it is syphoned off.

Drying and Weighing the Lead Dioxide.—The lead dioxide retains water with great tenacity,[2] and the results will be too high if the regular factor—0·8662—for converting the lead dioxide into the equivalent amount of metallic lead be employed. Classen recommended drying the lead dioxide at 180–190°, and Hollard at 200°. Smith has shown that deposits of lead dioxide approximately 0·5 grm. in weight do not really have a constant composition until they have been dried at 230°. For instance, with a deposit containing the equivalent of 0·4992 grm. of Pb:

Time heated . . .	30	30	30	30	30	min.
Temperature . . .	200°	200°	230°	240°	270°	
PbO_2	0·5788	0·5790	0·5780	0·5780	0·5780	grm.

Similarly, with the equivalent of approximately 0·25 grm. Pb, the lead dioxide attains a constant weight at 200°. In the former case, the factor of conversion corresponds with the empirical value 0·8634; and in the latter case, 0·8643. With still less quantities of the dioxide, say, 0·05 to 0·1 grm., a special factor is not needed. If the theoretical factor be used the results will be high. High results can be prevented by the use of empirical factors. Fischer recommends:

Amount of Pb .	Below 0·1	0·1	Bet. 0·1 and 0·3	0·5	1·0	grm.
Factor . . .	0·8660	0·8658	0·8652	0·8629	0·8610	

Instead of following this procedure, May[3] recommends gentle ignition of the dioxide at a low temperature to convert the dioxide into lead monoxide—PbO—before weighing. The results are then excellent. Thus, Treadwell gives for four experiments:

				Mean.
PbO_2 found . . .	0·2202	0·2200	0·2203	0·2202—0·2202 grm.
PbO found . . .	0·2042	0·2046	0·2043	0·2044—0·2044 grm.

According to J. G. Fairchild (*Journ. Ind. Eng. Chem.*, **3**. 902, 1911), the essential conditions for good deposits are: (1) hot solutions (50°–60°); and (2) an initial low amperage.

[1] To recognise the end of the electrolysis, withdraw a few drops of the solution from the dish; make the solution alkaline with ammonia; add a few drops of H_2S water, or ammonium sulphide, when a black or dark brown precipitation represents lead and shows that the electrolysis is not completed. Of course other recognised qualitative tests for lead are available. If the level of the electrolyte be raised a little by the addition of distilled water, the appearance of a yellow or orange film on the newly immersed surface of the anode also shows that the electrolysis is not ended.

[2] It is very doubtful if the excessive weight of the lead dioxide is due to the formation of a higher oxide. A. Hollard, *Bull. Soc. Chim.* (3), **29**. 151, 1903; (3), **31**. 239, 1904; *Compt. Rend.*, **136**. 229, 1904; *Chem. News*, **79**. 122, 1899; R. O. Smith, *Journ. Amer. Chem. Soc.*, **27**. 1287, 1905; R. C. Benner, *Journ. Ind. Eng. Chem.*, **2**. 348, 1910; J. G. Fairchild, *ib.*, **3**. 902, 1911; F. Utz, *Chem. Zeit.*, ii, 1788, 1912.

[3] W. C. May, *Amer. J. Science* (3), **6**. 255, 1873; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 148, 1911; H. J. S. Sand, *Chem. News*, **100**. 269, 1909.

In another series of trials the following average results were obtained:

Lead used in each trial	0·1898 grm.
Lead found by weighing as PbO_2	0·1907 grm.
Lead found by converting $PbO_2 \rightarrow PbO$	0·1898 grm.

Removing the Deposited Lead Peroxide from the Electrode.—Digest the dioxide with nitric acid to which a little hydrogen peroxide has been added (say, 1 c.c.). The lead dissolves rapidly and quickly. Smith recommends removing the deposit by the action of dilute nitric acid along with a rod of copper or zinc. Henz[1] recommends a solution of sodium or potassium nitrite acidified with nitric acid.

Preparation of Lead Sulphate for Electrolysis.—Lead is commonly separated as sulphate in gravimetric work. According to Classen, lead sulphate is brought into a condition for electrolysis by warming the precipitated lead sulphate with an excess of ammonia, whereby lead hydroxide is formed. Pour the mixture with constant stirring into a platinum dish containing about 20 c.c. of warm concentrated nitric acid. If any lead sulphate appears as a precipitate, it will soon dissolve in the solution. The solution is then ready for electrolysis.

Lead sulphate is also brought into a condition for electrolysis by dissolving it in ammonium acetate, adding 20 c.c. of concentrated nitric acid, and electrolysing the solution at 60° with a current density of 1·5 to 1·7 amps.[2]

Marie[3] places the lead sulphate in the dish to be used for the electrolysis; the dish is heated on the water bath along with some dilute nitric acid. Gradually add crystals of ammonium nitrate until all is dissolved. Every 0·3 grm. of lead sulphate requires 5 grms. of ammonium nitrate. Dilute the solution with warm water so that the liquid contains about 10 per cent. of free acid, and electrolyse the solution at 60–70°. For lead silicate, decompose the fine powder with sulphuric and hydrofluoric acids. Too great an excess of sulphuric acid prevents the solution of lead sulphate by the ammonium nitrate.[4]

Effect of Foreign Electrolytes.—The process indicated above will separate lead from the alkalies, alkaline earths, chromium, beryllium, zirconium, iron, uranium, zinc, nickel, cobalt, and cadmium. Chlorides should be absent from the electrolyte.[5] The determination of lead by this process in the presence of appreciable amounts of arsenic will be unreliable.[6] The results will be low. Classen says that "when enough (0·5 grm.) is present, no lead will be deposited as dioxide on the anode, but metallic lead mixed with arsenic will be deposited on the cathode. If the electrolysis be continued for some time, the arsenic will be gradually driven from the cathode as arsenic hydride, and the precipitated lead will pass into solution. Finally, if the electrolysis be sufficiently prolonged, all the lead will be deposited as dioxide on the anode." The action of selenium is similar. According to Vortmann[7] the results are high in the presence of sulphuric, selenic, and chromic acids. Hence, he recommends reprecipitation by electrolysis. In the presence of arsenic and phosphorus the results will be low. In that case Vortmann recommends depositing the metal as lead on the cathode, dissolving the metal in nitric acid, and reprecipitating the lead as dioxide.

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[1] F. Henz, *Zeit. anorg. Chem.*, **37.** 2, 1903.

[2] H. Nissensen and B. Neumann, *Chem. Ztg.*, **19.** 1142, 1895.

[3] C. Marie, *Compt. Rend.*, **130.** 1032, 1900; *Chem. News*, **82.** 51, 1900.

[4] For lead chromate, Marie proceeds in a similar manner, but less ammonium nitrate is needed —2 grms. of ammonium nitrate suffice for 0·5 grm. of lead chromate.

[5] When chlorides are present, evaporation with sulphuric acid and treatment of the sulphate as described in the text will furnish a solution ready for electrolysis.

[6] B. Neumann, *Chem. Ztg.*, **20.** 382, 1896.

[7] G. Vortmann, *Liebig's Ann.*, **351.** 283, 1907. For the effect of gums, and colloids generally, see H. Freundlich and J. Fischer, *Zeit. Elektrochem.*, **18.** 885, 1912.

§ 162. The Rapid Deposition of Lead Dioxide by a Rotating Electrode—Exner's Process.

The enormous gain in the speed of deposition which attends the use of a rotating electrode removes one of the most serious objections to electro-analysis. In the case of copper, for example, a rotating anode enables a satisfactory determination to be made in 5 minutes, using a current of 10 volts and 13 amps.; nickel, in 15 minutes; cobalt, in half an hour; cadmium, in 5 minutes; etc. The following diagram (fig. 132), after Fischer, emphasises very forcibly the great gain in time obtained by the use of rotating electrodes. The ordinates show the amounts of copper precipitated by rotating and stationary electrodes after the elapse of different intervals of time (abscissæ).

Knobukow[1] introduced rotating electrodes in electro-analysis in 1886, but the subject did not attract much attention until the American chemists—Gooch and Smith—took up the subject about 1903. These chemists and their co-workers extended Knobukow's idea, and showed that a still further gain in time attends the use of currents of greater density and voltage. For further details see the works cited on page 256.

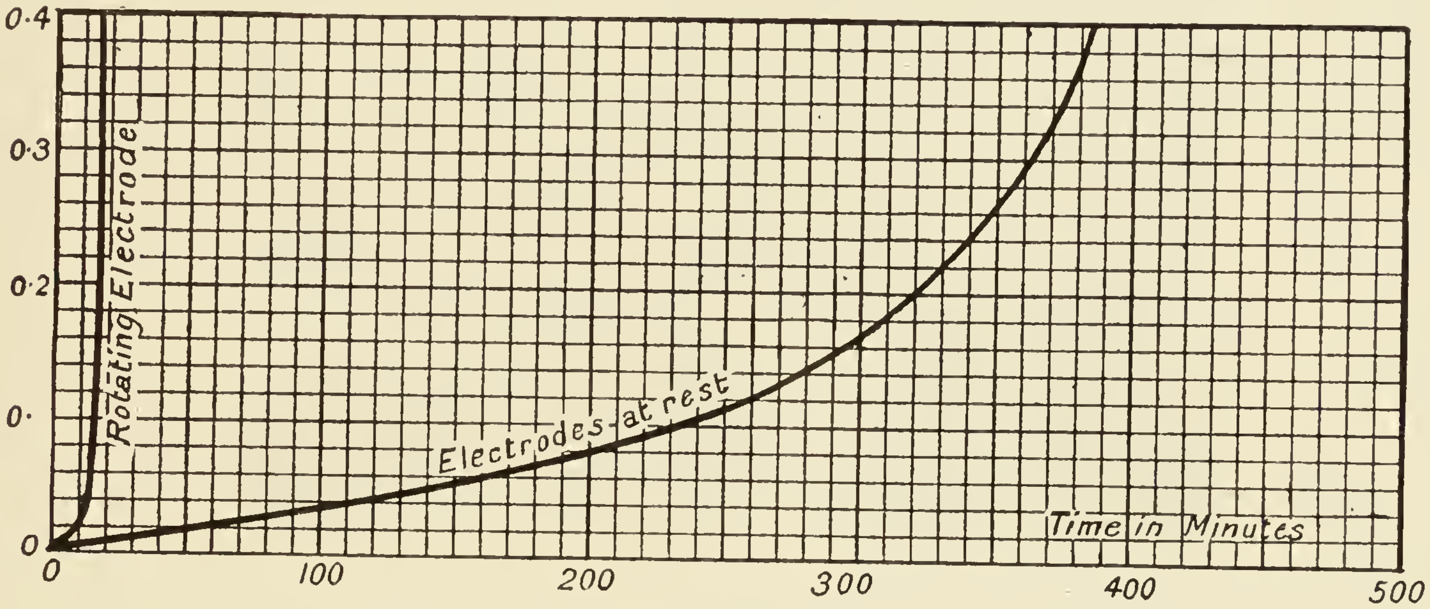

Fig. 132.—Time of deposition, stationary and rotating electrodes.

The Apparatus.—The determination of lead as dioxide by the use of rotating electrode may now be described, on the assumption that pages 253 to 262 have been mastered. Fit up the apparatus illustrated in fig. 133—the lettering is similar to that in figs. 117 and 118, from which it differs in that the platinum dish is here used as the anode, not the cathode. The current accordingly passes through the electrolytic cell in the reverse direction to what was the case with copper. The disc electrode is replaced by a spiral of heavy platinum wire with the spirals fixed in position by twisted platinum binding wires. The centre of the spiral is depressed to give it the form of a shallow bowl about 5 cm. in diameter. This electrode is clamped to the axis of a wheel which can be rotated by a motor or turbine between 450 and 600 revolutions per minute, and yet be in electrical contact with the battery.[2]

The Electrolysis.—The solution, prepared as indicated in the preceding section for stationary electrodes, is placed in a platinum basin, matted on its inner surface. Add 20 c.c. of concentrated nitric acid and dilute the solution to make a total volume of 110–125 c.c. Heat the solution to about 70°, and start the electrode rotating at about 500 revolutions per minute.[1] A current of electricity at 4–5 volts, and current density 10–11 amps., is passed through the solution. The lead will soon be deposited as a black adherent velvety film of dioxide on the dish. The maximum period required for 0·25 grm. of the metal was found by Smith to be 15 minutes; and for 0·5 grm., 25 minutes.[2] Smith found that the rate of precipitation from a solution containing the equivalent of 0·5787 grm. of PbO_2 was as follows:—

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[1] N. von Knobukow, *Journ. prakt. Chem.* (2), **33**. 473, 1886; F. A. Gooch and H. E. Medway, *Amer. J. Science* (4), **15**. 320, 1903; F. F. Exner, *Journ. Amer. Chem. Soc.*, **25**. 896, 1903; R. O. Smith, *ib.*, **27**. 1287, 1905.

[2] Numerous types of cells for rotating electrodes have been devised—some are described in the text-books indicated on page 256. That described in the text may be the simplest but not necessarily the best when many determinations have to be made.

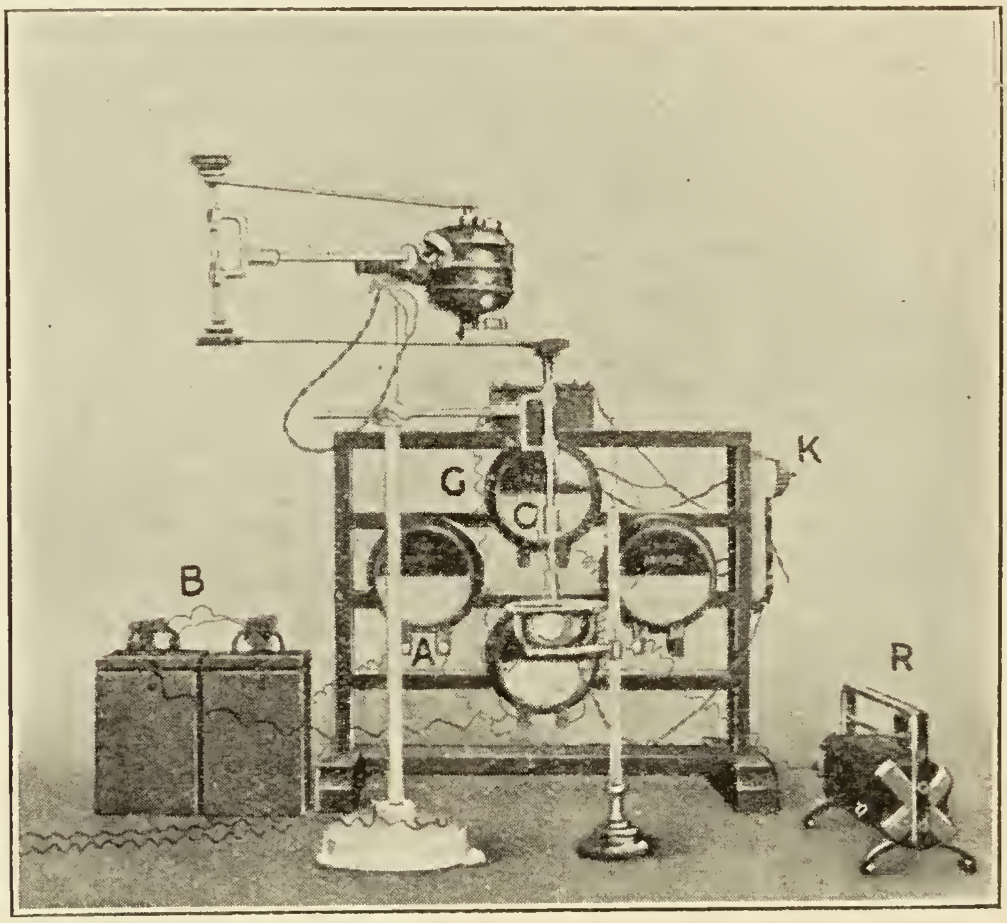

Fig. 133.—Electrolysis by rotating electrode.

Time	5	10	15	20	25	30	min.
PbO_2	0·4940	0·5708	0·5747	0·5770	0·5787	0·5789	grm.

In about 25 minutes, when the decomposition is finished, stop the rotator, and reduce the current by the introduction of resistance. Add water to cover the lead peroxide; syphon off water from the dish while the dish is kept full of water. Wash the deposit with alcohol and ether in the usual manner.

To illustrate the results which might be expected:

PbO_2 found	0·0566	0·1137	0·2887	0·5781	0·5788	grm.
Pb (by factor 0·8662) . .	0·0490	0·0985	0·2501	0·5008	0·5015	grm.
Pb (used)	0·0491	0·0982	0·2496	0·4992	0·4996	grm.

The calculation of the amount of lead corresponding with the deposited lead dioxide here presents the same difficulty as was encountered in dealing with stationary electrodes. The factor 0·8662 furnishes too high results.

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[1] There is no need to heat the solution during the electrolysis, because the high current used keeps the liquid hot. With higher speeds the electrolyte may sweep round the edge of the dish and be thrown against the cover glass. This will do no particular harm if the amount of liquid in the basin does not exceed 125 c.c.

[2] F. F. Exner, *Journ. Amer. Chem. Soc.*, **25**. 896, 1903; R. O. Smith, *ib.*, **27**. 1287, 1908.

§ 163. The Colorimetric Determination of Lead.

Pelouze[1] first proposed to estimate small amounts of lead in a given solution from the intensity of the brown coloration[2] produced when the lead is converted into sulphide.[3] The method has been frequently used for estimating the small amounts of lead in water, citric acid, etc.[4] The method has also been recommended for the determination of the amount of lead in factory dusts, glazes, etc.[5] The results are usually too low in presence of traces of free acid—acetic or hydrochloric acid—since some lead is not then converted into the sulphide. This will be obvious from our study of the action of hydrogen sulphide on lead salts in acid solutions (page 273). The results are very much better in alkaline solutions using sodium or ammonium sulphide as precipitant.

Influence of Iron Salts.—Dark brown iron sulphide is precipitated in alkaline solutions, and since traces of iron are nearly always associated with lead, it is necessary to eliminate the disturbing effects produced by this agent. Warington used the colorimetric process for estimating small quantities of lead in citric and tartaric acids, and, in order to avoid the effects produced by iron, he recommends making the solution "alkaline with ammonia, treating the solution with a few drops of potassium cyanide, and heating it to near the boiling point." The iron is thus converted into a complex cyanide—probably ferrocyanide—and it is not then affected by the subsequent addition of alkaline sulphide. The method works quite satisfactorily provided the iron is all present in the ferrous condition, and the liquid is strongly alkaline. Ferric salts are not converted by the treatment with potassium cyanide into colourless substances unaffected by alkaline sulphides. It is therefore necessary to reduce ferric salts to the ferrous condition before applying the test. Wilkie recommends sodium thiosulphate in acid solution as a reducing agent. Its action is probably represented by the equation :—$2Na_2S_2O_3 + 2FeCl_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl$.

The Determination.—Wilkie made an artificial mixture of 12 grams of citric acid, 0·004 grm. of ferric iron, 0·00005 grm. of lead. This mixture was placed in a "Jena flask and made up to about 35 c.c. with water. 2 c.c. of $\frac{1}{10}$N-sodium thiosulphate[6] were then added, and the whole heated to incipient boiling, and the flame removed. After about 5 minutes, the solution became perfectly water-white, and to it was immediately added 1 c.c. of a 10 per cent. solution of potassium cyanide,[1] and then[2] an excess (13 c.c.) of 0·880 ammonia, and the whole gently boiled until colourless."

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[1] T. J. Pelouze, *Ann. Chim. Phys.* (3), **79.** 108, 1841.

[2] It is possible to detect 1 part of lead per 16,000 parts of solution, according to F. Jackson (*Journ. Amer. Chem. Soc.*, **25.** 992, 1903); 1: 26,900, according to T. G. Wormley; and 1: 1,000,000, according to A. B. Prescott and E. C. Sullivan, and R. Warington (*Journ. Soc. Chem. Ind.*, **12.** 97, 1893); C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 1824 ; J. L. Lassaigne, *Journ. Chim. Méd.*, **8.** 581, 1832 ; P. Harting, *Journ. prakt. Chem.* (1), **22.** 45, 1841

[3] A. Trillat (*Compt. Rend.*, **136.** 1205, 1903) showed that lead peroxide produces a blue coloration in contact with tetramethyl-diamidodiphenylmethane in a solution acidified with acetic acid. By converting the lead into peroxide, and estimating the amount of the latter from the intensity of the blue coloration, the results are far from satisfactory. Similar attempts to convert the lead into peroxide and subsequently bringing the peroxide in contact with a solution of potassium iodide and estimating the amount of lead from the intensity of the colour of the liberated iodine—in the presence and in the absence of starch—likewise failed to give constant results without an abnormal expenditure of time in isolating the lead peroxide.

[4] J. M. Wilkie, *Journ. Soc. Chem. Ind.*, **28.** 636, 1909 ; R. Warington, *ib.*, **12.** 97, 1893 ; C. A. Hill, *Chemist Druggist*, **66.** 388, 1905 ; H. W. Woudstra, *Zeit. anorg. Chem.*, **58.** 168, 1908 ; F. L. Teed, *Analyst*, **17.** 142, 1892 ; E. R. Budden and H. Hardy, *ib.*, **19.** 169, 1894 ; B. Kühn, *Arbeit. Kais. Gesand.*, **23.** 389, 1906 ; A. G. V. Harcourt, *Journ. Chem. Soc.*, **97.** 841, 1910 ; M. Lucas, *Bull. Soc. Chim.* (3), **15.** 39, 1896 ; A. Liebrich, *Chem. Ztg.*, **22.** 225, 1898 ; G. Bischof, *Zeit. anal. Chem.*, **18.** 73, 1879 ; V. Antony and T. Benelli, *Gazz. Chim. Ital.*, **1.** 218, 1871 ; **2.** 194, 1872 ; P. Carles, *Journ. Pharm. Chim.* (6), **12.** 517, 1900 ; L. Libermann, *Pharm. Centralhalle*, **29.** 10, 1889. L. W. Winkler, *Zeit. angew. Chem.*, **26.** 38, 1912, recommends addition of ammonium chloride to get more reliable results.

[5] H. R. Rogers, *Report Departmental Committee appointed to inquire into the Dangers incident on the Use of Lead*, **2.** 118, 1910 ; A. G. V. Harcourt, *ib.*, **2.** 120, 1910. Rogers's method cannot be regarded seriously as a quantitative process.

[6] It is very necessary to test all reagents to ensure their freedom from traces of lead—ammonia, sodium hydroxide, etc.

Assuming that the solution under investigation is treated as the mixture just described, a similar solution is made with a known amount of lead. This solution is systematically diluted with water in Nessler's glasses, and one drop of ammonium sulphide[3] added to each. The colours so obtained are compared with that of the solution under investigation in the usual way—see Colorimetry.[4]

Disturbing Factors.—Woudstra found that with the colorimetric process:

Lead present	0·001	0·001	0·0009	0·0009	grm.
Estimated lead in error . .	−18	−8	+11·1	−3·3	per cent.

It must be borne in mind that the lead sulphide precipitated in alkaline solution is colloidal,[5] and that the tint is to some extent determined by the size of the colloidal particles, which, in turn, is dependent upon the nature of the salts in the solution under investigation, and on slight variations in the way the solution has been prepared. Vigorous agitation, for instance, may coagulate the suspended colloid and cause a precipitation of the lead sulphide. Salts of the alkalies and alkaline earths rapidly coagulate the colloidal sulphide. According to Kühn, barium chloride is 100 times more active than sodium nitrate in coagulating the suspended colloid.

Sometimes the colloidal sulphide imparts a smoky opalescence to the solution. This is not favourable for satisfactory comparisons. Warington recommended the addition of (approximately) an equal volume of glycerol to the solution under investigation; and Harcourt recommended mixing the solution with about one-fifth its volume of a clear solution of cane sugar (half sugar, half water), in order to eliminate this difficulty. Each of these additions makes the tint of the lead sulphide slightly paler, and less opaque, and thus facilitates the work of comparison.

The effect of iron has been already discussed. In the case of lead glazes, cobalt oxide may have been added to the glaze, or dissolved from the body by the glaze. Cobalt salts in alkaline sulphide solutions give a dark brown coloration (page 386), which would make the reported amount of lead too high.[6]

To summarise: In order to get reliable results it is necessary that the solutions under comparison have the same general character—otherwise the result may be over 50 per cent. in error. With unknown solutions, this can only be assured by elaborate preparations which occupy so much time that the main advantage of the colorimetric process—rapidity of execution—is nullified.

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[1] It is best to use an excess of potassium cyanide, say 25 of potassium cyanide to 1 of iron.

[2] Wilkie considers that the results are better if the potassium cyanide is added to the acid solution before the ammonia, since the formation of the ferrocyanide proceeds faster in the acid solution.

[3] According to Warington, ammonium sulphide is a more delicate reagent than hydrogen sulphide.

[4] A. G. V. Harcourt (*Journ. Chem. Soc.*, **97**. 841, 1900) makes a series of permanent colour standards matching the tints of solutions containing variable amounts of lead. The colour standards are made from mixtures of ferric, cobalt, and copper sulphates in suitable proportions. These are labelled and preserved in hermetically sealed glass cylinders. J. W. Lovibond (*Measurement of Light and Colour Sensations*, London, 124, 1910) made combinations of his standard glass slips to match the tints of solutions containing known amounts of lead.

[5] W. Spring, *Bull. Acad. Roy. Belg.*, 483, 1909.

[6] G. D. Elsdon (*Pharm. Journ.* (4), **89**. 143, 176, 1912) points out that in filtering very dilute solutions of lead salts part of the lead may be retained by the filter paper. If lead solution be acidified with 0·6 per cent. acetic acid the absorption does not occur, and the lead may be washed from the paper by 0·6 per cent. acetic acid.

CHAPTER XXV.

THE DETERMINATION OF BISMUTH AND MERCURY.

§ 164. The Separation of Mercury from Lead, Bismuth, Copper, and Cadmium—Rath's Process.

As indicated on page 279, mercuric sulphide is almost insoluble in ammonium sulphide, but readily soluble in sodium or potassium sulphides. If, therefore, the sulphides precipitated by hydrogen sulphide be digested with an alkaline sulphide, the mercury will be found with the arsenic and antimony group. Indeed, mercury, tin, arsenic, and antimony sulphides can be sharply and conveniently separated from lead, silver, bismuth, and copper sulphides by digesting the mixed sulphides in a mixture of potassium sulphide and hydroxide.[1] If cadmium (and zinc) should be present, the mercury sulphide is but imperfectly dissolved.[2] The net result of this operation is a solution containing tin, mercury, arsenic, and antimony sulphides, and a precipitate containing copper, lead, and bismuth sulphides—assuming that cadmium is absent. If tin also be absent, this method of analysis offers some advantages, because the mercury can be readily separated from the arsenic and antimony by treating the solution with ammonium chloride. If tin be present, much tin will be precipitated with the mercury, and the separation by this process is inconvenient.

If the sulphides precipitated by hydrogen sulphide be digested in ammonium sulphide,[3] a good separation can be made in the absence of tin and copper. Mercury, bismuth, lead, copper, and cadmium will remain with the insoluble residue, while arsenic and antimony, with some copper sulphide, will be dissolved. If tin be present, a somewhat soluble compound of tin and mercury sulphide appears to be formed, because part of the mercury sulphide will pass into solution, and part of the tin will remain with the precipitate.[4]

The plan of analysis must, therefore, be modified to suit these different conditions. Fortunately, mercury is comparatively rare in silicate analysis, and one of the two distillation processes indicated later, or simply "loss on ignition" of the original sample, will suffice. Rath's process[5] is one of the most convenient for separating mercury from the sulphides insoluble in ammonium monosulphide.

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[1] Prepared by saturating half the prepared volume of a 15 per cent. solution of potassium hydroxide with hydrogen sulphide. Mix the two parts, and filter after the solution has stood for some days (*cf.* page 277).

[2] K. Bülow, *Zeit. anal. Chem.*, **31**. 697, 1892; *Chem. News*, **67**. 174, 1893.

[3] Ammonium Monosulphide.—Saturate three volumes of aqueous ammonia (sp. gr. 0·88) with hydrogen sulphide, and add two volumes of fresh ammonia (sp. gr. 0·88) to the saturated solution. (Ammonium polysulphide is made by dissolving 25 grms. of "flowers of sulphur" in a mixture of 500 c.c. of ammonium monosulphide and 500 c.c. of water.) When mercury is present, the freshly prepared colourless ammonium sulphide is used in place of sodium monosulphide, for the reasons stated on page 279—E. Donath, *Chem. Ztg. Rep.*, **15**. 68, 1895.

[4] T. Wilm, *Ber.*, **20**. 232, 1887.

[5] G. von Rath, *Pogg. Ann.*, **96**. 322, 1855.

It is based on the fact that the mercuric sulphide is insoluble in boiling dilute nitric acid (sp. gr. 1·2–1·3),[1] while the remaining sulphides—silver,[2] bismuth, copper, cadmium, and lead—pass into solution. A little insoluble lead sulphate may be formed by the action of the nitric acid on the sulphide. The mercuric sulphide can then be separated from the lead sulphate by digesting the mixture with a little aqua regia; dilute the solution with water, filter off the precipitated sulphur and lead sulphate, and wash with water. A trace of lead sulphate may be dissolved by the filtrate. This is recovered later. The mercury is separated as sulphide by Volhard's process.

§ 165. The Gravimetric Determination of Mercury as Sulphide—Volhard's Process.

In this process[3] the mercury is precipitated as sulphide by the addition of ammonium sulphide to a nearly neutral solution; the mercuric sulphide is dissolved in caustic alkali, from which it is reprecipitated as mercuric sulphide, by the addition of ammonium nitrate.

Precipitation of the Mercuric Sulphide.—Almost neutralise the acid filtrate from the preceding operation with sodium carbonate; add a slight excess of colourless ammonium sulphide (freshly made, page 341); and, finally, with constant agitation, a solution of pure sodium hydroxide. When the dark colour begins to lighten, heat the solution to boiling, and add more sodium hydroxide until the liquid is perfectly clear.[4] The mercury dissolves forming a thio-salt—$Hg(SNa)_2$. Add an excess of ammonium nitrate, and boil the solution as long as ammonia is given off. The thio-salt is decomposed by the ammonium nitrate:

$$Hg(SNa)_2 + 2NH_4NO_3 = 2NaNO_3 + (NH_4)_2S + HgS.$$

Wash the precipitated mercuric sulphide[5] two or three times with hydrogen sulphide water, then with hot water by decantation through a Gooch's crucible until the water no longer reacts with silver nitrate. Transfer the precipitate to the crucible, dry between 110° and 112°,[6] and weigh as mercuric sulphide—HgS. Every gram of the mercuric sulphide represents 0·8618 gram of mercury, or 0·9305 gram mercuric oxide—HgO. The results are generally a little high owing to the presence of some sulphur with the precipitate.[7]

Removal of Sulphur from Metallic Sulphides.—The sulphur may be removed either by boiling the precipitate with a little sodium sulphite before filtering so as to convert the sulphur into soluble sodium thiosulphate ($S + Na_2SO_3 = Na_2S_2O_3$), or by extraction with carbon disulphide.[1] The following are convenient methods of conducting the process of extraction:—The Gooch's crucible containing the mixture is placed on a glass tripod whose feet rest on the bottom of a beaker containing some carbon disulphide. The beaker is covered with a round-bottomed flask containing cold water. The beaker, etc., is placed on a hot-water bath.[2] The carbon disulphide boils at 46°, and, after condensing against the bottom of the flask, drops into the crucible and passes back to the bottom of the beaker. Wiley's or Drehschmidt's extraction apparatus[3] is convenient for washing precipitates free from sulphur by extraction with carbon disulphide. Both have a receptacle, *A*, for the Gooch's crucible below a condenser, *C*; Drehschmidt's is shown in fig. 134. A current of cold water is passed through the condenser, and the flask, *B*, containing the solvent, etc., is placed in a hot-water bath, or supported over an incandescent electric lamp. The carbon disulphide boils, and the condensed liquid runs through the crucible back to the bottom of the flask. In about half an hour the apparatus is allowed to cool, and the carbon disulphide is washed from the precipitate in the crucible by one treatment with alcohol, and

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[1] J. Torrey, *Amer. Chem. Journ.*, 7. 355, 1886; J. L. Howe, *ib.*, 8. 75, 1886. Mercuric sulphide is not appreciably attacked by boiling dilute nitric acid, but a single drop of dilute hydrochloric acid (1 : 3) will convert black mercuric sulphide into a yellow compound, and if a few drops of hydrochloric acid be present, some of the mercury will pass into solution. Hence, the nitric acid must be perfectly free from chlorides and hydrochloric acid.

[2] If silver be present, it will be precipitated as chloride by the hydrochloric acid.

[3] J. Volhard, *Liebig's Ann.*, 255. 255, 1889.

[4] A precipitate of insoluble lead sulphate may be present owing to the dissolution of some lead sulphate in the aqua regia. If present, it must be filtered off and the precipitate washed with dilute sodium hydroxide. The lead sulphate is mixed with that previously obtained, and treated by the method of page 317.

[5] The precipitate so obtained is much more compact and easily filtered than mercuric sulphide precipitated by hydrogen sulphide.

[6] The time of drying is materially lessened by a final washing with alcohol—R. S. M'Bride, *Journ. Phys. Chem.*, 14. 189, 1910.

[7] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2. 140, 1911; L. Vignon, *Compt. Rend.*, 116. 584, 1893.

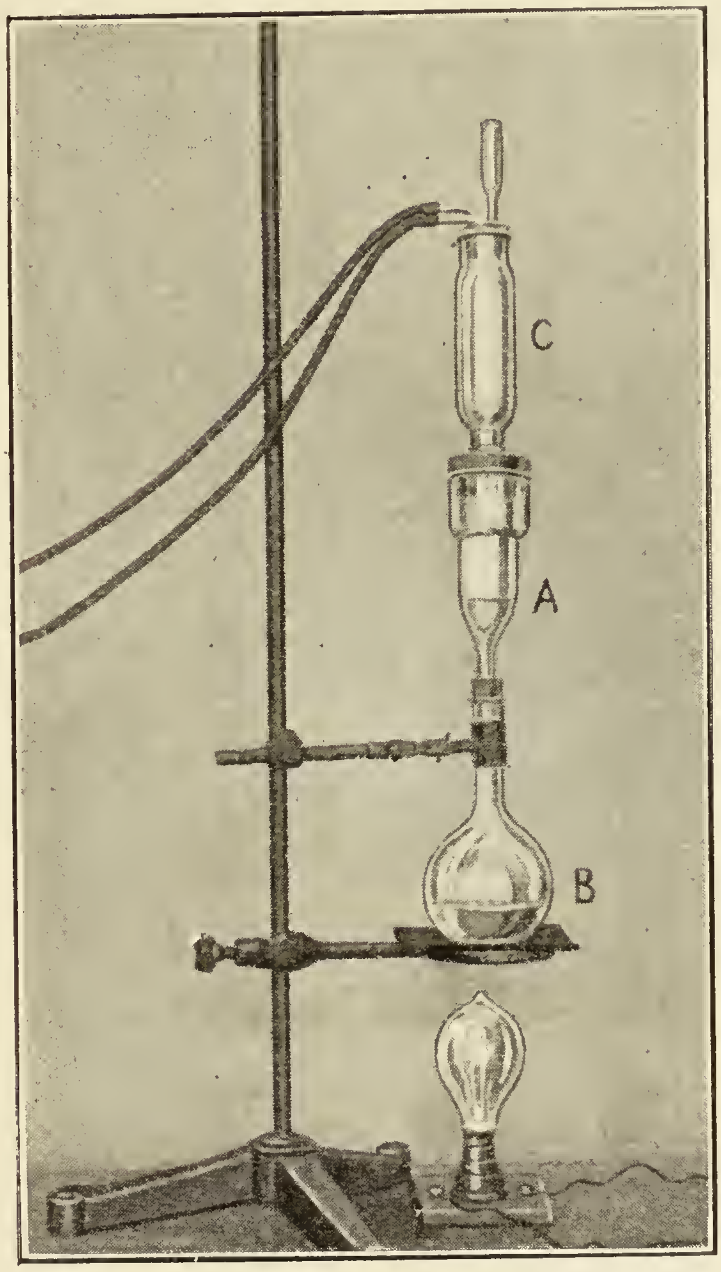

Fig. 134.—Extraction apparatus.

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[1] C. Friedheim and P. Michaelis, *Zeit. anal. Chem.*, 34. 526, 1895; H. W. Wiley, *ib.*, 23. 586, 1884; G. Vortmann, *Uebungsbeispiele aus der quantitativen chemischen Analyse*, Leipzig, 33, 1910.

[2] Note, no naked flames must be near enough to risk ignition of the carbon disulphide.

[3] H. W. Wiley, *Journ. Anal. App. Chem.*, 7. 65, 1893; W. D. Richardson and E. F. Scherubel, *Journ. Ind. Eng. Chem.*, 4. 220, 1912; H. J. C. Curr, *ib.*, 4. 535, 1912.

one treatment with ether. Dry the sulphide at 110°, and weigh as indicated above. The results are very fair, generally less than 0·1 per cent. low.

§ 166. The Distillation Process for Mercury.

Erdmann and Marchand's Process.

All mercury compounds,[1] with the exception of the iodide, are quantitatively decomposed when heated with quicklime. The reaction, in the case of the chloride, is represented :

$$HgCl_2 + CaO = CaCl_2 + OHg.$$

Hence, it is often most convenient to determine the mercury on a separate sample by a distillation process, and ignore the mercury when the other constituents are determined, because the mercury compound which might contaminate a precipitate is volatilised when the precipitate is ignited before weighing.

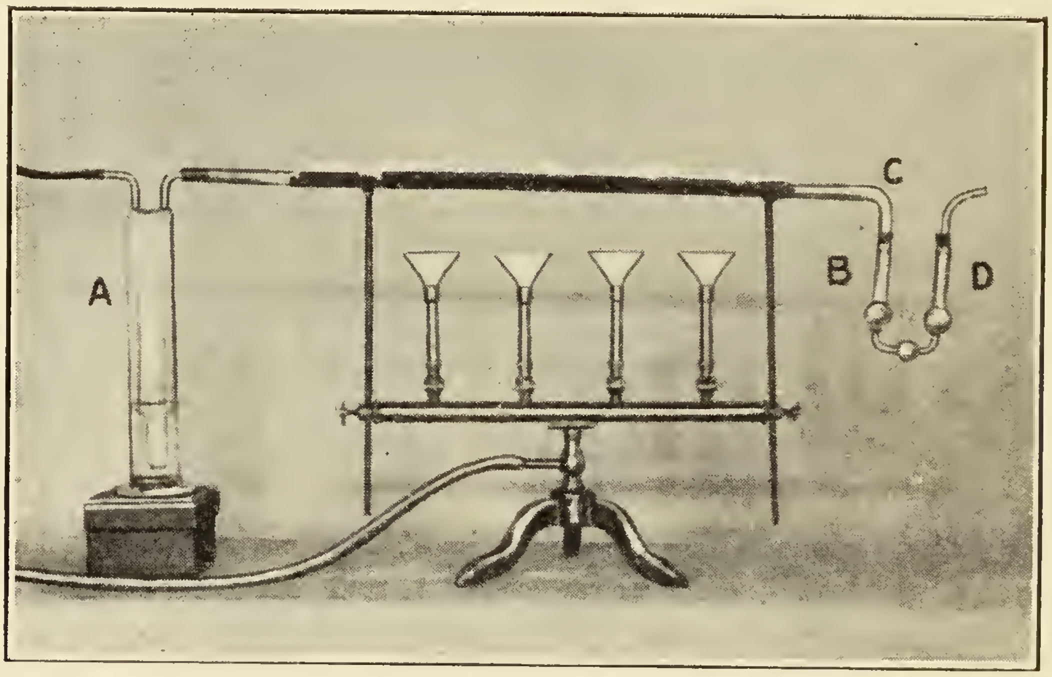

FIG. 135.—Erdmann and Marchand's distillation process for mercury.

Mercury can be determined in colours containing, say, mercuric chromate, and in gold amalgams, "best" gold, etc., by placing a plug of asbestos at the end of a combustion tube—45 to 50 cm. long, and 1·5 cm. wide—then an 8-cm. layer of freshly burned calcium oxide ; a 10-cm. layer of an intimate mixture of a weighed quantity of the given substance with an excess of calcium oxide ; a 20-cm. layer of calcium oxide ; and, finally, a loose plug of asbestos fibre.[2] Bend the tube as shown in the diagram, *C*, fig. 135. Fit the bent end of the combustion tube, by means of a piece of rubber tubing, with one arm of a small Péligot's tube, *B*, as shown in the diagram. The other arm of the Péligot's tube, *D*, is loosely packed with pure gold leaf. The other end of the combustion tube is connected with a wash-bottle, *A*, containing sulphuric acid, and with a tube delivering coal gas. The coal gas is allowed to bubble through the apparatus at the rate of about three bubbles per second for about half an hour. Gradually raise the temperature of the combustion tube, starting with the 20-cm. layer, and gradually carry the flame backwards until finally the whole tube is being heated at the same time. The part *C* of the combustion tube can be heated with a naked Bunsen's flame, and any mercury here condensed is thus driven forward into the Péligot's tube, but the rubber connection must not be scorched. The current of coal gas is continued all the time the combustion is in progress, and while the apparatus is cooling. Most of the mercury collects in the lower bulb of the Péligot's tube; a small part is arrested by amalgamation with the gold leaf;[1] and some of the mercury may condense in the narrow portion of the combustion tube near *C*. The Péligot's tube is disconnected[2] and a current of air, dried by passing through a drying tower, fig. 164, is passed through the apparatus for about half an hour. Weigh the Péligot's tube; the increase in weight represents mercury derived from the given sample. Now cut the combustion tube where the mercury is condensed. Weigh. Heat this portion of the combustion tube while a current of air is passed through. This volatilises the mercury. Cool the tube in a desiccator and weigh again. The apparent loss in weight represents the mercury which was condensed in the tube. Add this to the preceding result to get the total mercury.[3]

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[1] A simple determination of the "loss on ignition" is sometimes sufficient for the mercury in a dry sample of mercury chromate. The last trace of mercury is difficult to expel from gold—M. J. Personne, *Compt. Rend.*, **56**. 63, 1862.

[2] The tube is often closed at one end, and the closed end is packed with magnesite or sodium bicarbonate, which, on heating towards the end of the operation, evolves a stream of carbon dioxide ; this drives out the mercury vapour. The mercury is collected in water. The results are satisfactory with rich (7–8 per cent. mercury) ores.

Holloway's Modification of Eschka's Process.

This method is based on the fact that when mercuric sulphide is heated with iron filings, iron sulphide and volatile mercury are formed.[4] The mercury is condensed on a gold or silver plate, and an amalgam is formed. The increase in the weight of the plate from this cause represents the amount of mercury in the sample. The process is used for sulphides and amalgams. The process can also be used with "best gold" and other amalgams.[5]

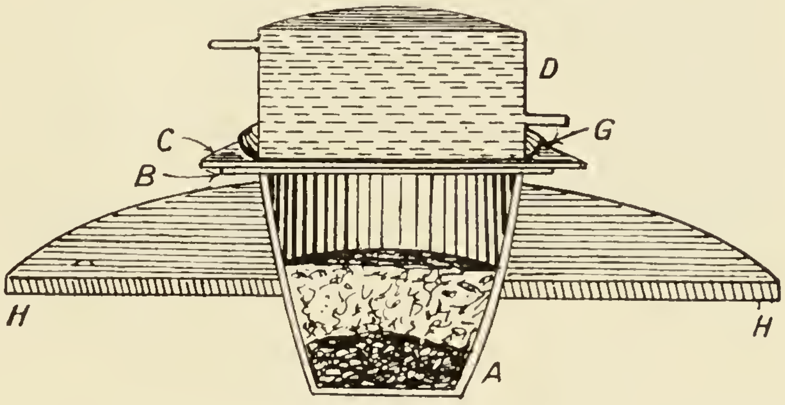

FIG. 136.—Holloway's apparatus.

The Apparatus.—The upper edge of a deep, glazed porcelain crucible—about 4 cm. diameter, and 4·5 cm. high—is ground flat. The crucible, *A*, figs. 136 and 137, is supported in a hole in an asbestos or quartz plate, *H*. A 5-cm. disc of silver[6] plate (weighing about 0·4–0·5 grm. per sq. cm.) is annealed by holding it in the Bunsen's flame for a minute or two. The disc is rubbed between two flat surfaces until it lies perfectly flat on top of the crucible Weigh this disc, *B*. Place a rather larger metal disc, *C*, on top of the weighed disc, *B*, in order to keep the latter clean. A metal condenser, *D*, through which a current of cold water is flowing, is placed on the discs to keep them cool.

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[1] Instead of using gold leaf, etc., water is sometimes used in the bottom of the Péligot's tube; the combustion tube has one end closed, and a layer of magnesite is placed at the closed end.

[2] Watch that no mercury falls from the combustion tube after the Péligot's tube has been disconnected.

[3] H. Rose, *Pogg. Ann.*, **110**. 542, 1860; O. L. Erdmann and R. F. Marchand, *Journ. prakt. Chem.* (1), **31**. 385, 1844; C. R. König, *ib.* (1), **70**. 64, 1857; A. C. Cumming and J. Macleod, *Jour. Chem. Soc.*, **103**. 513, 1913.

[4] As in Jordan's test for mercury—W. J. Jordan, *Schweigger's Journ.*, **57**. 339, 1829.

[5] A. Eschka, *Chem. News*, **26**. 22, 1872; *Zeit. anal. Chem.*, **11**. 344, 1872; *Dingler's Journ.*, **204**. 47, 1872; C. T. Holloway, *Analyst*, **31**. 66, 1906; *Chem. Eng.*, **4**. 169, 1906; R. E. Chism, *Eng. Min. Journ.*, **66**. 480, 1898.

[6] Gold has a greater "collecting" power for the mercury than silver; but silver has the greater "collecting" power weight for weight, and is also a better heat conductor. Hence Holloway recommended silver, Eschka and Chism used gold.

The condenser is held in place by a 500-grm. weight, *W*, on top of the condenser. A gutter, *G*, runs round the bottom of the condenser to collect any condensed moisture trickling down the condenser.[1] The moisture is removed from time to time by means of a piece of blotting paper.

Charging the Crucible.—The finely powdered (120's lawn) and dry[2] sample is weighed[3] into the crucible and mixed with 10 grms. of fine iron filings.[4] The mixture is covered with 5 grms. of the coarse iron filings. Everything is placed in position, as shown in the diagrams, figs. 136 and 137.

Volatilisation of the Mercury.—The crucible is heated with a small flame sufficient to raise the bottom of the crucible to redness without the flame coming in contact with the sides of the crucible.[5] After heating from 20 to 30 minutes, let the system cool for 15 minutes with the condenser at work. Wash the gold or silver disc with alcohol;[6] dry in a desiccator; and weigh. The apparent increase in weight of the disc represents the mercury. It requires a little practice to adjust the size of the flame and the time of heating to be sure all the mercury is volatilised under the conditions just indicated.[7] To make quite sure, reheat the crucible with a fresh gold or silver disc in position. If all the mercury was volatilised during the first heating, there will be no increase in weight of the disc. If any increase in weight is obtained, add the result to the mercury obtained with the first plate. The plates can be freed from mercury, and prepared for another determination, by simply heating them to drive off the mercury.[8] A determination occupies 40 to 50 minutes.

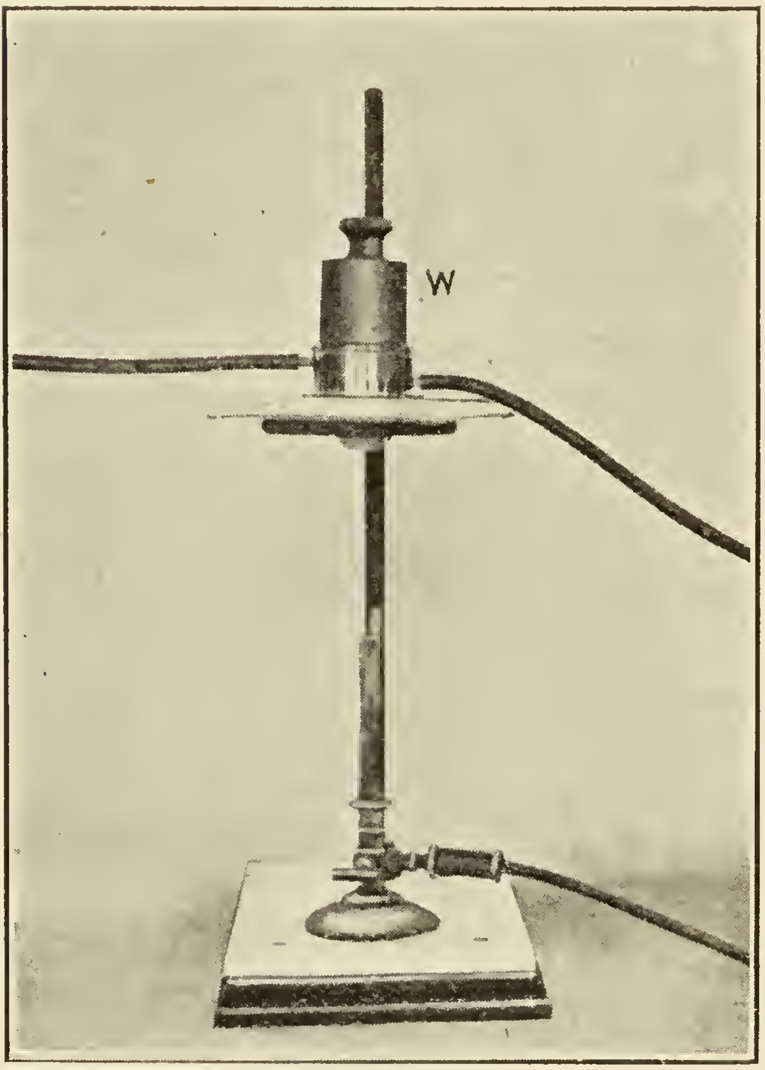

Fig. 137.—Holloway's apparatus.

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[1] The whole outfit can be bought for about 5s.

[2] If metallic mercury be present, the drying must be conducted with care on account of the tendency of mercury to volatilise.

[3] If the amount of mercury in the sample is less than 1 per cent., take 2 grms. of the sample; if between 1 and 2 per cent., take 1 grm.; if between 2 and 5 per cent., take 0·5 grm.; and if over 5 per cent. is present, grind the sample with 10 grms. of dry sand (120's lawn), and take an aliquot portion so as to keep approximately within the indicated limits.

[4] Clean iron filings free from oils and fats are prepared by heating the filings to redness for an hour in a covered crucible. Sift the filings through an 80's lawn, and also sift some through a 30's lawn. Keep each in a separate bottle.

[5] The tip of a small Méker's flame is very suitable. The plate does not absorb mercury well if it is hot.

[6] To remove tarry and organic matters, etc., which might have collected on the gold or silver plate. The gold amalgams used in pottery, if already mixed with "fat oil," should be washed with ether to remove the oil before treatment by this process.

[7] If the plate does not show a clear circular stain, either too much ore has been used, or the lid did not fit properly. If the stain extends beyond the edge of the crucible, there will be an element of uncertainty owing to the probable loss of mercury. The plate and crucible should fit close enough to prevent this.

[8] The plate seems to improve with use, since it gets more porous and absorbs mercury better.

Special Precautions.—(1) Avoid the excessive heating of the crucible; the edge of the foil should never feel warm to the fingers. (2) The silver or gold foil should be thoroughly cleaned and fit on the crucible quite flat. (3) The foil and cooler should be carefully adjusted to ensure contact all round the top of the crucible. (4) The foil should be quite dry. (5) Draughts are objectionable. (6) Allow 15 minutes for cooling before removing the foil to prevent danger of losing uncondensed mercury vapour.

Duplicate determinations on a 1-per cent. ore should agree to within 0·05 per cent. (Holloway), a result which cannot be equalled by the wet method.

§ 167. The Separation of Bismuth from Lead, Cadmium, and Copper—Löwe's Process.

Löwe[1] has based a process on the fact that water converts bismuth nitrate into an insoluble basic salt under conditions where lead, copper, and cadmium salts undergo no such transformation:

$$Bi(NO_3)_3 + 2H_2O \rightleftharpoons Bi(OH)_2NO_3 + 2HNO_3.$$

The basic nitrate is washed with a solution of ammonium nitrate; this allows the precipitate to be washed without decomposition. If water alone be used, the precipitate becomes more and more basic, the filtrate consequently acquires an acid reaction, and some bismuth passes into solution. The process can, however, be used for the separation of bismuth from the elements just named.[2]

Precipitation.—The nitric acid solution of the sulphide is evaporated on a water bath to a syrupy consistency, and mixed with hot water and thoroughly stirred with a glass rod. Take care to loosen any crusts which may have formed on the sides of the basin. The solution is again evaporated, and the addition of water and the evaporation are repeated until further addition of water produces no turbidity—three or four evaporations usually suffice. This shows that the reaction indicated above is complete. Evaporate the solution to dryness, and when the dry mass has ceased to smell of nitric acid, cool.

Washing.—Add a cold solution of ammonium nitrate (2E), and after standing some time with frequent agitation to make sure that all the lead nitrate has passed into solution, filter. Wash the precipitate with the solution of ammonium nitrate, and dry in an air bath.

Ignition.—Remove the dry precipitate from the filter paper, and preserve it in a watch-glass. Ignite the filter paper in a porcelain crucible at a low temperature. Moisten the ash with nitric acid. Evaporate to dryness very cautiously to prevent spurting. Transfer the precipitate to the crucible and ignite filter-paper ash and precipitate together. Try to keep the temperature below the fusing point of the oxide, since, if the temperature be too high, the oxide melts and attacks the glaze.[3] When the weight has become constant, weigh the precipitate as bismuth oxide—Bi_2O_3.

Purification of the Bismuth Oxide.—The precipitate may be contaminated with a little iron, mercury, and copper if these elements be present. Hence, some prefer to redissolve the precipitate before ignition and repeat the separation. The combined filtrates are evaporated to dryness and calcined at a low temperature to destroy the ammonium salts, which interfere with the subsequent precipitation of the lead as sulphate (page 317).

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[1] J. Löwe, *Journ. prakt. Chem.* (1), 74. 344, 1858; C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 1821.

[2] This process can be used for evaluating bismuth nitrate and bismuth oxide. The latter is soluble in nitric acid.

[3] The error from this cause can be neglected in most cases. If reducing gases be present inside the crucible, some of the oxide will be partially reduced.

If sulphuric or hydrochloric acid be present, a basic sulphate or chloride may be formed, which is not converted to oxide on ignition. The results will accordingly be high. In that case, Rose[1] recommends fusing the mass for about 15 minutes with four or five times its weight of, say, 98 per cent. potassium cyanide in a covered crucible. When all is fused the crucible is gently tapped to collect the little beads of metal into one button. The crucible should not be heated above low redness. Wash the cold mass with water to remove the cyanides and cyanates. The button is then washed with alcohol, dried at 100°, and weighed as metallic bismuth. This weight multiplied by 1·1154 gives the corresponding amount of bismuth oxide—Bi_2O_3.[2]

§ 168. The Separation of Bismuth from Copper and Cadmium—Jannasch's Process.

The bismuth can be separated[3] from copper and cadmium, if cadmium be present, by evaporating a solution containing salts of these elements to dryness. Dissolve the residue in, say, 5 c.c. of nitric acid (sp. gr. 1·4) and 25 c.c. of water, and pour the solution into a beaker containing 25 c.c. of concentrated ammonia, and 50 c.c. of a 4 per cent. solution of hydrogen peroxide, with constant stirring. A dull yellow precipitate of basic bismuth hydroxide separates.[4] Let the precipitate settle; decant the clear; add more of the ammoniacal hydrogen peroxide; decant; transfer to a filter paper; wash with hot dilute ammonia (1 : 8), and finally with hot water, until a drop of the wash-water gives no precipitate when evaporated on a piece of platinum foil.

To remove any copper or cadmium which might be precipitated with the bismuth, dissolve the precipitate on the filter paper in hot dilute nitric acid; evaporate to dryness, and repeat the precipitation as described above.

After complete washing, dry the precipitate at 90°–95°; ignite it in a porcelain crucible until its weight is constant; and weigh as Bi_2O_3. The ignition of the precipitate, etc., is described in detail, page 347.[5]

§ 169. The Determination of Bismuth Colorimetrically.

Small amounts of bismuth are conveniently determined colorimetrically. Bismuth iodide[6] forms an intense yellow, orange, or red coloration,[7] which, unlike the somewhat similar colour by iodine, is not destroyed by sulphur dioxide. The process is not often used, and in consequence it has not been subjected to that critical examination which would have been the case had it been in common use. The use of comparatively large amounts of glycerol is an objectionable feature in the process.

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[1] H. Rose, *Pogg. Ann.*, **91**. 104, 1854; **110**. 136, 426, 1860.

[2] Sometimes the bismuth forms a kind of metallic lustrous film inside the crucible.

[3] P. Jannasch, *Zeit. anorg. Chem.*, **8**. 302, 1895; *Leitfaden der Gewichtsanalyse*, Leipzig, 107, 110, 1904; P. Jannasch and E. von Cloedt, *Zeit. anorg. Chem.*, **10**. 398, 1895; *Chem. News*, **72**. 64, 1895.

[4] If lead were present, it too would be precipitated with the bismuth as a peroxide.

[5] A. L. Benkert and E. F. Smith's process (*Journ. Amer. Chem. Soc.*, **18**. 1055, 1896; A. F. V. Little and E. Cahen, *Analyst*, **35**. 301, 1910), by precipitation as bismuth formate, is an excellent process for the separation of bismuth from lead, cadmium, etc.

[6] F. Field, *Chem. News*, **36**. 260, 1877; F. A. Abel and F. Field, *Journ. Chem. Soc.*, **14**. 290, 1862; M. Planes, *Chem. News*, **89**. 10, 1904; *Journ. Pharm. Chim.* (6), 385, 1903; L. L. de Koninck, *Bull. Soc. Chim. Belg.*, **19**. 91, 1905; F. B. Stone, *Journ. Soc. Chem. Ind.*, **6**. 416, 1887; T. C. Cloud, *ib.*, **23**. 523, 1904.

[7] One part of bismuth per 10,000 parts of water gives an orange colour; 1 part of bismuth in 40,000 parts of water, a light orange; and 1 part of bismuth in 100,000, a perceptible yellow coloration—T. C. Thresh, *Pharm. Journ.*, 641, 1880.

Test Solution.—The sample under investigation is dissolved in a flask with just sufficient nitric acid and water. Add 10 c.c. of glycerol and 10 c.c. of potassium iodide[1] solution, and make the solution up to 50 c.c. with glycerol. Place this solution in one test glass of the colorimeter.

Standard Solution.—Mix 10 c.c. of a standard solution of bismuth[2] with 10 c.c. of the potassium iodide solution, and make the solution up to 50 c.c. with glycerol and water.

Comparison.—The solutions may then be compared in the colorimeter. The solutions to be compared would have approximately the same concentration. Hence, it may be necessary to alter the amounts of standard and test solution indicated in the text. The calculations are made in the usual manner (pages 200 and 206).

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[1] POTASSIUM IODIDE SOLUTION.—Dissolve 5 grms. of potassium iodide in 5 c.c. of water, and make the solution up to 100 c.c. with glycerol.

[2] STANDARD SOLUTION OF BISMUTH NITRATE.—Dissolve 1 grm. of bismuth in 3 c.c. of nitric acid (sp. gr. 1·39) and 2·8 c.c. of water. Make the solution up to 100 c.c. with glycerol. The object of the glycerol is to keep the bismuth iodide in solution. The glycerol need not be used when dealing with small amounts of bismuth—say, 0·0001 to 0·0075 grm. per c.c. For larger amounts of bismuth use the glycerol.

CHAPTER XXVI.

THE DETERMINATION OF COPPER AND CADMIUM.

§ 170. Rivot's Thiocyanate Process for Copper.

THE very valuable electrolytic process for copper has been described on page 258. This will not do in the presence of cadmium. If cadmium be present, Rivot's process[1] of separation may be used. This depends upon the fact that an alkaline thiocyanate produces a precipitate of cuprous thiocyanate—$CuSCN$—in neutral or feebly acid solutions of a copper salt in the presence of a reducing agent. The solution is best slightly acidified with sulphuric or hydrochloric acid. An excess of acid is injurious. The solution should be free from oxidising agents—nitric acid, free chlorine oxides, etc. The process enables copper to be quantitatively separated from cadmium, and, indeed, many other metals.[2]

The Precipitation.—The solution[3] is neutralised with ammonia, if necessary; acidified with a couple of drops of sulphuric acid; and treated with an excess of sulphur dioxide, or ammonium bisulphite.[4] Then add, drop by drop, with constant stirring, an aqueous solution of ammonium thiocyanate. The greenish precipitate of mixed cuprous and cupric thiocyanates soon becomes white. Let the mixture stand overnight.

Washing and Drying the Precipitate.—Filter the solution, with the bulky precipitate, through a Gooch's crucible, previously dried and weighed; and wash with cold water[5] until the washings give but a faint red coloration with a solution of ferric chloride.[6] Then wash six times with 20 per cent. alcohol.

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[1] L. E. Rivot, *Compt. Rend.*, **38**. 868, 1854; R. G. von Name, *Zeit. anorg. Chem.*, **31**. 92, 1902; *Chem. News*, **83**. 258, 1901; E. Busse, *Zeit. anal. Chem.*, **17**. 53, 1878; **30**. 122, 1891; H. Tamm, *Chem. News*, **24**. 91, 1874; E. Fleischer, *ib.*, **19**. 206, 1869; G. Fernekes and A. A. Koch, *Journ. Amer. Chem. Soc.*, **27**. 1224, 1905; W. Hampe, *Chem. Ztg.*, **17**. 1691, 1893; *Journ. Soc. Chem. Ind.*, **13**. 421, 1894; B. Blount, *Analyst*, **19**. 92, 1894.

[2] Copper may be also separated from cadmium (Pb, Mg, Mn, Hg, Zn, etc.) by the nitroso-β-naphthol process, as indicated on page 394—G. von Knorre, *Zeit. anal. Chem.*, **28**. 234, 1889; and from cadmium, nickel, cobalt, aluminium, chromium, etc., by ammonium nitroso-phenylhydroxylamine—ammonium "cupferron"—as indicated on page 455.

[3] Remaining after the separation of the bismuth.

[4] Made by saturating aqueous ammonia with sulphur dioxide. Some use for the precipitation a mixture of 120 grms. of potassium thiocyanate and 120 grms. of sodium hydrogen sulphite dissolved in 2 litres of water (H. Tamm, *l.c.*).

[5] The precipitate is practically insoluble in cold, but appreciably soluble in hot water.

[6] The copper in the thiocyanate may be determined volumetrically with some advantage if the standard solutions are ready made. E. Fleischer (*Chem. News*, **19**. 206, 1869) digests the precipitate in a solution of caustic alkali and washes the red precipitate of cuprous oxide with hot water until the washings give no red coloration with ferric chloride, and determines the copper by Haen's process (page 351). S. W. Parr (*Journ. Amer. Chem. Soc.*, **22**. 685, 1900; **24**. 580, 1902; H. A. Guess, *ib.*, **24**. 708, 1902; W. E. Garrigues, *ib.*, **19**. 940, 1897; R. K. Meade, *ib.*, **20**. 610, 1898; *Chem. News*, **80**. 67, 1899; J. Volhard, *Liebig's Ann.*, **190**. 251, 1877) dissolves the precipitated thiocyanate in 10 c.c. of a solution of potash (10 per cent.), adds 10 c.c. of ammonia (sp. gr. 0·96), and titrates with potassium permanganate until the

Dry the precipitate between 110° and 120°; and weigh as CuSCN. The drying must be repeated until the weight is constant.[1] The weight of the precipitate multiplied by 0·6541 gives the corresponding amount of cupric oxide—CuO.

Accuracy of the Results.—The results are excellent. For example, with known amounts of copper, Fernekes and Koch found:

Copper (taken) . . .	0·0939	0·0939	0·0939	0·0188	0·0188	grm.
Copper (found) . . .	0·0941	0·0939	0·0939	0·0189	0·0188	grm.

The main objections to the method are the slight solubility of the precipitate in an excess of the precipitating reagent, and in water; and the tardy separation of the precipitate. The method can be used to separate copper from zinc, cadmium, iron, cobalt, nickel, bismuth, tin, arsenic, and antimony, because these elements are not precipitated under the conditions of the experiment.

If desired, the precipitate can be roasted to drive off the cyanogen compounds; the residue dissolved in acid, and the copper determined volumetrically; or the thiocyanate can be dissolved in about 2 c.c. of concentrated nitric acid, boiled for a few minutes, treated with an excess of ammonia and the excess boiled off, treated with 2 to 3 c.c. of acetic acid, and the solution titrated with iodine as described below. Not more than 0·0001 grm. of copper will be found in the filtrate with cadmium—if that element be present.

§ 171. De Haen's Volumetric Iodine Process for Copper.

E. de Haen's process[2] is based on the fact that when an excess of potassium iodide is added to a concentrated solution of a copper salt, acidulated with acetic acid, cuprous iodide is formed, and an equivalent amount of iodine is liberated. The amount of free iodine is determined by titration with sodium thiosulphate. If the solution be too dilute, the cuprous iodide produced in the reaction just indicated re-forms the original salt. The "back reaction" proceeds as the

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green colour persists after warming the solution at 45°–55°—for a short time. Then add an excess of the permanganate solution—say one-third or one-fourth of the amount already added. Let the mixture stand five minutes. Acidify the solution with 25 c.c. of dilute sulphuric acid (1 : 2), and titrate with permanganate at 60°–70° until the pink coloration appears. One gram of potassium permanganate corresponds with 0·7193 grams of cupric oxide—CuO.

[1] Cuprous thiocyanate begins to decompose if heated above 170°. A. Claus (*Journ. prakt. Chem.* (1), **15**. 401, 1838) found 3·0 per cent. of water in a sample dried at 115°; and M. Meitzendorff (*Pogg. Ann.*, **56**. 63, 1842) found 1·54 per cent. when dried at 100°. Practically all the water is removed by working as described in the text.

[2] E. de Haen, *Liebig's Ann.*, **91**. 237, 1854; A. Rümpler, *Journ. prakt. Chem.* (1), **105**. 193, 1868; M. Flajolet, *ib.* (2), **11**. 105, 1894; D. Vitali, *Zeit. anal. Chem.*, **36**. 549, 1897; L. Moser, *ib.*, **43**. 597, 1904; **44**. 196, 1904; E. V. Videgren, *ib.*, **48**. 539, 1909; F. M. Litterscheid, *ib.*, **41**. 219, 1902; *Chem. Ztg.*, **33**. 263, 1909; E. Victor, *ib.*, **29**, 179, 1905; F. M. Litterscheid, *ib.*, **33**. 263, 1909; G. Vortmann and J. von Orlowsky, *Zeit. anal. Chem.*, **20**. 416, 1881; *Monats. Chem.*, **7**. 418, 1886; M. Willenz, *Rev. Chim. Anal. App.*, **5**. 355, 1896; *Chem. News*, **76**. 243, 1897; L. Garnier, *Journ. Pharm. Chim.* (6), **9**. 326, 1899; F. Pisani, *Compt. Rend*, **47**. 294, 1858; M. Haupt, *Pharm. Centr.*, **10**. 509, 1899; *Chem. News*, **70**. 206, 1894; L. de Bruyn, *Rec. Chim. Pays-Bas*, **10**. 119, 1891; H. Cantoni and M. Rosenstein, *Bull. Soc. Chim.* (3), **35**. 1069, 1906; P. Gerlinger, *Zeit. angew. Chem.*, **19**. 520, 1906; L. Moser, *Zeit. anorg. Chem.*, **56**. 143, 1907; *Chem. Ztg.*, **31**. 77, 1907; G. Fernekes and A. A. Koch, *Journ. Amer. Chem. Soc.*, **27**. 1224, 1905; R. S. Dulin, *ib.*, **17**. 346, 1895; A. H. Low, *ib.*, **18**. 457, 1896; **24**. 1082, 1902; *Chem. News*, **74**. 52, 1896; A. M. Fairlie, *Eng. Min. Journ.*, **78**. 787, 1905; A. H. Low, *ib.*, **59**. 124, 1896; E. H. Miller, *ib.*, **81**. 519, 1906; P. E. Browning, *Amer. J. Science* (3), **46**. 280, 1893; F. H. Heath, *ib.* (4), **25**. 513, 1908; F. A. Gooch and F. H. Heath, *ib.* (4), **24**. 65, 1907; *Chem. News*, **97**, 174, 187, 1908; E. O. Brown, *Journ. Chem. Soc.*, **10**. 65, 1857; J. W. Walker and M. V. Dover, *ib.*, **87**. 1584, 1905; R. Williams, *Chem. News*, **58**. 273, 1888; J. W. Westmoreland, *ib.*, **58**. 78, 1888; *Journ. Soc. Chem. Ind.*, **5**. 48, 1886; U. Tsukakoski, *Eng. Min. Journ.*, **90**. 969, 1910; F. E. Lathe, *ib.*, **93**. 1071, 1912; A. W. Peters, *Journ. Amer. Chem. Soc.*, **34**. 422, 1912; W. C. Bray and G. M. J. MacKay, *ib.*, **32**. 1193, 1910.

separated iodine is removed by the sodium thiosulphate to produce the phenomenon of "after-blueing";[1] and it is retarded by increasing the concentration of the potassium iodide. This shortens the time required for the titration. Free mineral acids react with the potassium iodide, forming hydriodic acid. A little free acid does no particular harm, but if much acid be present, some cuprous iodide is dissolved. This acts as a catalytic agent, accelerating the oxidation of the hydriodic acid by atmospheric oxygen. This leads to "after-blueing" and to high results.

The Preparation of the Solution.—If the copper has been precipitated as thiocyanate (or sulphide), the precipitate is digested with, say, 5 c.c. of nitric acid until the solution of the copper is complete. Evaporate the solution on a water bath with hydrochloric acid in order to expel the red fumes of nitrogen oxides.[2] Let the solution cool. Redissolve the residue in 25 c.c. of water, and neutralise the acid by the addition of a few drops of ammonia.[3] Boil the solution in order to expel the ammonia. Add 2 c.c. of concentrated acetic acid in order that the acid may be in slight excess.[4] If necessary, boil to ensure the complete dissolution of the copper. The cold solution occupies about 50 c.c. If not, make the solution up to this volume with water.

The Titration.—Dissolve 3 grms. of potassium iodide in the solution.[5] Nearly white cuprous iodide separates and iodine is liberated. Shake the solution vigorously. The reaction is represented by the equation:

$$2Cu(C_2H_3O_2)_2 + 4KI \rightleftharpoons Cu_2I_2 + I_2 + 4KC_2H_3O_2.$$

The free iodine which separates colours the solution brown. The solution should be cold, and kept cold, in order to prevent loss of iodine. To avoid oxidation, etc., titrate the solution *at once* with a standard solution of sodium thiosulphate[6] until the brown colour of the iodine has changed to a faint straw yellow.[7] Then add a couple of drops of a cold solution of starch (page 286) to develop the "iodine blue," and continue the titration cautiously, drop by drop, until the iodine blue is discharged. A drop in excess will suffice. The action of the thiosulphate on the iodine is represented by the equation:

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[1] When the blue colour of the starch iodide has been removed by the sodium thiosulphate, and more iodine passes into solution, the blue starch iodide colour will again appear. If this blue reappears after the colour has once been discharged by the titration, the phenomenon is called "after-blueing."—J. H. Davies and E. P. Perman, *Chem. News*, **93**. 225, 1906; K. Sugiura and P. A. Kober, *Journ. Amer. Chem. Soc.*, **34**. 818, 1912.

[2] This is very important. A. H. Low (*l.c.*) recommends the addition of 5 c.c. of bromine water and boiling the solution until the bromine is expelled in order to ensure the removal of the nitric acid; E. C. Kendall (*Journ. Amer. Chem. Soc.*, **33**. 1947, 1911) recommends boiling with sodium hypochlorite and afterwards taking up the free chlorine with phenol.

[3] Or sodium bicarbonate, not the carbonate (page 290). Note that iodine may be carried off if much carbon dioxide escapes from the solution after the addition of the potassium iodide.

[4] Avoid a large excess of acetic acid. The solution should not contain more than 3 c.c. of nitric, hydrochloric, or sulphuric acid, or 25 c.c. of 50 per cent. acetic acid, per 100 c.c. of solution. For the action of hydrochloric acid on sodium thiosulphate titrations, see J. T. Norton, *Amer. J. Science* (4), **7**. 287, 1899; *Chem. News*, **80**. 27, 1899. S. U. Pickering (*Journ. Chem. Soc.*, **37**. 135, 1880) showed that more iodine is required to oxidise the thiosulphate as the proportion of hydrochloric acid increases.

[5] Or add about 6 c.c. of a solution of potassium iodide containing 50 grms. of the solid per 100 c.c.; that is, 1 c.c. contains about half a gram of the solid. An excess of potassium iodide does no harm; too little will make the subsequent titration tedious owing to the gradual solution of precipitated iodine. An excess is therefore necessary to keep the precipitated iodine in solution. A "supra-excess," of course, means waste, and potassium iodide is expensive.

[6] STANDARD SOLUTION OF SODIUM THIOSULPHATE.—Dissolve 12 grms. of the pure anhydrous salt in a litre of pure, recently boiled distilled water. If the crystalline salt is used, take 19 grms. The latter is first reduced to powder and dried between sheets of blotting paper. After the solution has stood about a fortnight, it is standardised by weighing 0·10, 0·15, and 0·20 grm. of pure electrolytic copper foil separately in three 250-c.c. Erlenmeyer's flasks. Warm the copper with 5 to 10 c.c. of nitric acid (sp. gr. 1·20). Make the volume of the solution in each flask up to about 25 c.c., and evaporate on a steam bath in order to expel red fumes of nitrogen oxides. Then treat each solution as indicated in the text.

[7] If the end point does not appear before 25 c.c. of the thiosulphate have been added, add 2 grms. more potassium iodide.

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6.$$

The blue colour of the starch iodide returns on exposure to the atmosphere. If the solution remains colourless two minutes, the titration may be considered finished.

If 1 c.c. of the standard solution of sodium thiosulphate represents 0·0159 grm. of copper oxide, and 25 c.c. of the sodium thiosulphate solution be required for the titration, then the solution under investigation contained the equivalent of $25 \times 0·0159 = 0·3975$ grm. of copper oxide.

Influence of Foreign Substances.—If the blue colour of the starch iodide, after a titration, returns almost immediately, and this again after the addition of two more drops of thiosulphate, the titration will probably be unreliable owing to the presence of oxidising agents—probably arising from the incomplete expulsion of the red fumes of nitrogen oxides at an earlier stage of the operation. Excessive dilution, excessive amounts of acetic acid, and the presence of sodium or ammonium acetates retards the reaction between the copper acetate and the potassium iodide. This leads to low results. Hence the care recommended above to remove the ammonia. In the presence of these retarding agents, the titration is somewhat tedious, since the "after-blueing" has to be followed up for a long time. The presence of a large amount of alkaline salts—particularly sulphates and nitrates—leads to wrong results.

Ferric acetate liberates iodine from potassium iodide; ferric phosphate does not. Hence, if a little iron be present, some recommend the addition of sodium phosphate.[1] If much iron be present, the copper should first be separated as sulphide, metal, or thiocyanate. Bismuth does not interfere beyond obscuring the end point and making it difficult to recognise when the reaction is complete. Too much thiosulphate may accordingly be run in before the starch is added. Bismuth forms a brown-coloured iodide which is very like the colour of the iodine in solution. Bismuth also imparts a dirty green colour to the starch indicator, so that the change is not from blue to colourless, but from dirty green to yellowish white. Lead, arsenic, and antimony interfere[2] with the determination, and should be removed before titrating.[3] Lead may be removed as sulphate, bismuth as phosphate, or both as peroxides by ammonium persulphate in alkaline solution (page 348).

Errors.—The chief points requiring attention are:—(1) Errors due to the use of insufficient potassium iodide; (2) too much acid liberates iodine from potassium iodide in presence of air, but sufficient acid must be present to give a prompt liberation of iodine and a sharp end point during the titration—sulphuric and acetic acids can be used; nitric and hydrochloric acids are not so good; (3) loss of iodine by volatilisation (page 300); (4) the solution to be estimated should occupy as small a volume as possible and be titrated with the most dilute thiosulphate solution which will give a good end point; and (5) the end point is modified in the presence of a large excess of cuprous iodide.

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[1] L. Moser (*Zeit. anal. Chem.*, **43**. 597, 1904) adds an excess of sodium pyrophosphate —$Na_4P_2O_7$—to determine copper in the presence of arsenic and iron by the iodine process. Complex phosphates are formed; of these, the copper salt is alone decomposed by acetic acid.

[2] According to Fernekes and Koch, cadmium, zinc, aluminium, arsenic, antimonic and stannic salts do not interfere.

[3] C. and J. J. Beringer, *A Textbook of Assaying*, London, 201, 1908.

The mixture of starch and cuprous iodide, just before the end point is reached, assumes a chocolate-brown coloration, and this changes to a pale buff colour with the last necessary drop of thiosulphate. The end point has occurred when another drop of thiosulphate does not diminish the prevailing light tint of the mixture. So long as a drop of thiosulphate falling on the quiet surface of the liquid being titrated produces a perceptible white area, the end point has not been reached.

§ 172. The Evaluation of Copper Oxide and Carbonate.

Dissolution of the Copper Oxide.—Digest, say, 0·5 grm. of the oxide or carbonate on a hot plate with sulphuric acid; or with 6 to 10 c.c. of nitric acid and 7 c.c. of sulphuric acid, until the volatile acids are expelled. Heat the solution until sulphuric acid fumes begin to come off. Calcined copper oxide dissolves rather slowly, while copper oxide which has not been calcined at a high temperature dissolves quickly. When cold, add 25 c.c. of water;[1] and, if necessary, filter.

Precipitation of the Copper.—Place two strips of metallic aluminium[2]—say, 15 cm. by 2·5 cm. by 1 mm.—in the solution so that one end of each strip rests against the side of the beaker. Metallic copper is precipitated. Heat the solution to boiling. Cover the beaker with a clock-glass to prevent loss by spurting.[3] When all the copper is precipitated—about a quarter of an hour—transfer the liquid to a second beaker. Decant through a 9-cm. filter paper. Wash the copper[4] on the aluminium plates with a weak solution of hydrogen sulphide in air-free water to prevent oxidation of the copper. Wash the copper in the second beaker in the same manner. Reject the filtrate and washings.[5]

Dissolution of the Copper.—Place the second beaker containing the copper below the funnel. Put 5 to 6 c.c. of nitric acid (sp. gr. 1·3) in the first beaker, to dissolve the copper from the aluminium plates, and pour the acid solution through the filter paper; collect the solution in the beaker containing the copper below the funnel. Warm the solution until the copper is all dissolved. Wash the beaker and the filter paper. Expel the excess of acid, and treat the solution as described under de Haen's process (page 351).

Errors.—The Committee of the American Chemical Society, "On Uniformity in Technical Analysis,"[6] reported in 1904 that the following numbers represent the extremes sent in by nineteen analysts for a sample of cupriferous slag:—

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[1] Copper is slightly soluble in concentrated sulphuric and hydrochloric acids; hence, the acidity of the solution should be feeble.

[2] D. Tommasi, *Bull. Chim. Soc.* (2), **37**. 443, 1882; *Chem. News*, **46**. 62, 1882; A. H. Low, *Journ. Amer. Chem. Soc.*, **18**. 458, 1896; G. E. Perkins, *ib.*, **24**. 478, 1902; *Chem. News*, **86**. 86, 1902; E. V. Videgren, *Zeit. anal. Chem.*, **48**. 539, 1909. For magnesium: A. Villiers and F. Borg, *Compt. Rend.*, **116**. 1524, 1893. For zinc: G. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 269, 1822; F. Mohr, *Zeit. anal. Chem.*, **1**. 143, 1862; C. Ullgren, *ib.*, **7**. 442, 1868; F. Field, *Chem. News*, **1**. 62, 73, 1860. For cadmium: A. Classen, *Journ. prakt. Chem.* (1), **96**. 259, 1865. For iron: A. A. Julien, *Chem. News*, **26**. 9, 1871 (page 188). The iron should dissolve uniformly without the separation of black particles and the formation of ridges on the surface.

[3] Cadmium used in place of aluminium does not spurt so much. For magnesium, see E. G. Bryant, *Chem. News*, **76**. 30, 1897; S. A. Sworn, *ib.*, **76**. 59, 1897.

[4] The copper film has its own characteristic red colour. If the solution contained any arsenic or antimony, the copper will be contaminated and appear dirty brown.

[5] At this stage Field washed, dried, and weighed the metallic copper. He found that the copper precipitated by either zinc or iron always contained traces of these metals; at the same time, a small amount of copper in the primary solution always escapes precipitation. In commercial analyses, Field considers that the small amount of foreign metal precipitated with the copper compensates for that left in the primary solution.

[6] *Journ. Amer. Chem. Soc.*, **26**. 1644, 1904.

	SiO_2.	Fe.	Al_2O_3.	CaO.	MgO.	Zn.	Mn.	Cu.	S.
Highest . .	35·15	32·20	7·16	13·53	3·21	4·25	1·53	0·46	1·98
Lowest . .	31·27	30·33	3·24	10·73	1·00	1·87	0·11	0·20	1·45

The remarks made on the analyses of the argillaceous limestone, on page 248, are applicable here.

§ 173. The Colorimetric Determination of Copper—Carnelly's Process.

In cases where but small quantities of copper are likely to be present, in red lead, for example, the copper is usually determined colorimetrically,[1] from the intensity of the colour of ammoniacal solutions;[2] or from the intensity of the colour of ferrocyanide solutions.[3]

Potassium ferrocyanide, in acid solutions of copper, produces an earthy brown coloration which can be detected when 1 part of copper is present in 1,000,000 parts of solution. In neutral solutions, 1 part of copper can be detected in 1,500,000 parts of solution; and in neutral solutions containing ammonium nitrate, 1 part of copper can be detected in 2,500,000 parts of solution.[4] Hence, the ferrocyanide test is made with neutral solutions in the presence of ammonium nitrate. A similar result occurs if ammonium chloride be substituted for the nitrate.

The Standard Solution.—Pipette 1 c.c. of an aqueous solution of potassium ferrocyanide[5] into a 100-c.c. flask; add 5 c.c. of an aqueous solution of ammonium nitrate,[6] and make the solution up to 100 c.c. with distilled water. Transfer this solution, or an aliquot portion, to the right test glass of the colorimeter.

The Test Solution.—The solution under investigation must be neutralised.[7] If free potash be present, it is first neutralised and a slight excess of acid added, then a slight excess of ammonia. Boil off the excess of ammonia until the solution is neutral. If the solution is acid, add a slight excess of ammonia, and boil off the excess until the solution is neutral. Make the cold solution up to a definite volume, say, 100 c.c. Pipette 1 c.c. of the solution of potassium ferrocyanide into a 100-c.c. flask; add 5 c.c. of the ammonium nitrate solution, and then add an aliquot portion, say, 50 c.c., of the solution under investigation, and make the solution up to the mark with water. Transfer the whole solution, or an aliquot portion, to the left test glass of the colorimeter.

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[1] A. E. von Hubert, *Berg. Hütt. Ztg.*, **8**. 667, 1849; **10**. 804, 1851; V. Eggertz, *ib.*, **21**. 218, 1862; *Zeit. anal. Chem.*, **2**. 434, 1863; F. Dehms, *ib.*, **3**. 218, 1864; *Dingler's Journ.*, **172**. 160, 1864; G. Panten, *ib.*, **170**. 391, 1863; C. Stammer, *ib.*, **159**. 641, 1861; A. Payen, *ib.*, **27**. 372, 1828; V. A. Jacquelain, *Journ. prakt. Chem.* (1), **46**. 174, 1849; A. Müller, *ib.* (1), **60**. 474, 1853; *Zeit. anal. Chem.*, **2**. 434, 1863; M. Bergeron and L. l'Hôte, *Compt. Rend.*, **80**. 268, 1875; Wagmeister, *Oester. Zeit. Berg. Hütt.*, **13**. 270, 1865; J. Parry and J. J. Morgan, *Chem. News*, **67**. 259, 1893; T. P. Blunt, *ib.*, **32**. 3, 1875, **33**. 7, 1876; M. M. P. Muir, *ib.*, **33**. 11, 1876; M. W. Iles, *ib.*, **34**. 16, 1876; M. Lucas, *Bull. Soc. Chim.* (3), **19**. 815, 1898; *Chem. News*, **79**. 67, 1899; G. L. Heath, *Journ. Amer. Chem. Soc.*, **19**. 24, 1897; J. D. A. Smith, *Trans. Amer. Inst. Min. Eng.*, **30**. 851, 1901; L. W. Winkler, *Zeit. angew. Chem.*, **26**. 38, 1913.

[2] G. Bischof, *Dingler's Journ.*, **184**. 433, 1867; J. Milbauer and V. Stanek, *Zeit. anal. Chem.*, **46**. 644, 1907; A. Austin, *Min. World*, **33**. 753, 1910.

[3] T. Carnelly, *Chem. News*, **32**. 308, 1875.

[4] This is nearly the same delicacy as hydrogen sulphide, which gives a brown coloration with copper solutions when 1 part of copper is present in 2,500,000 parts of solution—A. Wagner, *Zeit. anal. Chem.*, **20**. 349, 1881. The ammonia test is one-tenth as sensitive as the ferrocyanide test—A. J. Cooper, *Journ. Soc. Chem. Ind.*, **5**. 84, 1886. The hydrogen sulphide reaction is not recommended for the colorimetric test because of the disturbing effects of lead, etc.

[5] POTASSIUM FERROCYANIDE SOLUTION.—Dissolve 1 grm. of potassium ferrocyanide in 25 c.c. of water.

[6] AMMONIUM NITRATE SOLUTION.—Dissolve 100 grms. of the salt in a litre of water.

[7] Free acids make the tint paler; free ammonia dissolves the precipitate produced by the ferrocyanide; and free potash decomposes it.

The Comparison.—Fill a burette with a standard solution of copper sulphate.[1] The burette may read to, say, $\frac{1}{50}$th c.c. Run the copper sulphate solution gradually from the burette into the right test glass of the colorimeter, with constant stirring, until the tints of the test solution and the standard solution are the same.

Calculations.—A gram of red lead furnished a solution which was made up to 100 c.c. 100 c.c. of the standard solution required 0·78 c.c. of the standard copper solution to produce uniformity of tint. The 0·78 c.c. of the standard copper solution contained 0·000078 grm. of copper oxide. Hence, 100·78 c.c. of the standard contain the same amount of copper oxide as the 100 c.c. of the given sample. Hence, the sample contains 0·0078 per cent. of copper oxide.

Accuracy of the Results.—The following results illustrate the accuracy of the process with solutions containing known quantities of copper oxide :—

Used . .	100	10	1·15	0·9	0·8	0·7	0·5	mgrm.
Found . .	102·01	11·2	1·19	0·91	0·82	0·71	0·52	mgrm.

The amount of copper oxide so determined is rather too high with the more concentrated solutions, but the results are quite good with small quantities.

Influence of Foreign Substances.—With moderate proportions, say, 0·25 to 2 c.c., an excess of the ferrocyanide does not affect the accuracy of the method. Similar remarks apply to the ammonium nitrate. For example, no difference could be detected by Carnelly in the results obtained with solutions containing 5 and 15 c.c. of the respective salt solutions. Ammonium chloride, sodium chloride, calcium chloride, calcium sulphate, magnesium sulphate, and sugar did not appear to affect the results. It is, however, best to destroy the organic matter, if present, by evaporation with nitric acid.

Influence of Lead.—Lead salts form a white precipitate with potassium ferrocyanide which does not interfere with a comparison of the colours. Carnelly made up a solution containing 2 grms. of lead nitrate (1·25 grms. Pb) with 0·255 grm. of copper nitrate in a litre of water. Varying proportions of this solution were taken, with the following results :—

Cu used	0·77	0·70	0·49	0·51	0·35	mgrm.
Cu found	0·80	0·75	0·51	0·49	0·38	mgrm.

Hence, small amounts of lead have no appreciable effect on the accuracy of the comparison.

Influence of Iron.—If iron be present, the solution is oxidised with a few drops of nitric acid and evaporated to a small bulk. Precipitate the iron with ammonia, filter, and wash. Redissolve the precipitate in nitric acid and reprecipitate with ammonia. Filter and wash. Mix the filtrates, and boil the solution to drive off the ammonia. The following represent the results obtained with varying amounts of iron,[2] which were separated before the copper was determined :—

Fe used	0	0·20	2·40	3·00	mgrm.
Cu used	0·66	0·51	0·61	0·76	mgrm.
Cu found	0·66	0·53	0·69	0·79	mgrm.

The results are therefore quite satisfactory.

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[1] STANDARD SOLUTION OF COPPER SULPHATE.—Dissolve 0·3138 grm. of pure copper sulphate—$CuSO_4 . 5H_2O$—in a litre of water. One c.c. of the solution contains 0·0001 grm. of CuO.

[2] Small amounts of iron are determined by the thiocyanate process (page 200).

§ 174. The Gravimetric Determination of Cadmium as Sulphate.

Precipitation as Cadmium Sulphide.—If any cadmium should be present, it will be found in the slightly acid filtrate from the copper thiocyanate. Treat the filtrate with hydrogen sulphide,[1] and cadmium sulphide,[2] more or less contaminated with basic salts,[3] will be precipitated.

Conversion of the Sulphide to Sulphate.—The sulphide is filtered; washed with water containing about 5 per cent. of ammonium nitrate; dissolved in hot hydrochloric acid (1 : 3); and heated on a water bath with a slight excess of sulphuric acid. The solution is then evaporated to dryness in the weighed platinum crucible supported over the ring burner (fig. 96), so that there may be no loss by spurting. The crucible is then placed in a larger crucible, and heated to redness[4] until no more white fumes of sulphuric acid are evolved. Cool in a desiccator. If the sulphate is tinged with a yellow colour, some oxide is present. In that case, add a drop of sulphuric acid to "moisten" the mass, and again ignite. Cool in a desiccator, and weigh as cadmium sulphate—$CdSO_4$. The cadmium sulphate so obtained should be white in colour, and dissolve to a perfectly clear solution in water.[5] Every gram of cadmium sulphate—$CdSO_4$—corresponds with 0·6159 gram of cadmium oxide—CdO. The results are excellent.[6] For instance, Follenius found with solutions containing 0·4036 grm of cadmium sulphate:

$CdSO_4$ found . . .	0·4036	0·4036	0·4033	0·4038	grm.
Error	0	0	−0·0003	+0·0002	grm.

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[1] The adjustment of the acid wants attention. The solution may contain between 2 and 7 c.c. of concentrated sulphuric acid per 100 c.c. If 100 c.c. of the solution contains more than the equivalent of 14 c.c. of hydrochloric acid (sp. gr. 1·11), the separation of cadmium sulphide will not be complete in the cold; and at 70°, more than 5 c.c. of this acid will lead to incomplete precipitation of the cadmium sulphide. No precipitate at all will be produced if over 22 c.c. of hydrochloric acid be present in 100 c.c. of the cold solution, and 19 c.c. in hot solutions (70°). The separation of cadmium sulphide is complete in dilute sulphuric acid (sp. gr. 1·19) in the cold. If but 5–40 c.c. of this acid be present in 100 c.c. of solution, the precipitate is finely divided and difficult to filter; with 40–70 c.c., the precipitate is more compact and easier to filter; and with 70–100 c.c. of this acid in 100 c.c. of solution the precipitation is complete, but the gas must be conducted through the solution a long time. In hot solutions (70°), if over 30 c.c. of this acid be present, traces of cadmium will remain in solution—O. Follenius, *Zeit. anal. Chem.*, **13**. 411, 1874.

[2] The colour of the precipitate is determined by the nature of the mother liquid, temperature, etc. The colour of the cadmium sulphide may vary from light yellow to an orange brown. N. von Knobukow, *Journ. prakt. Chem.* (2), **39**. 412, 1889; G. Büchner, *Chem. Ztg.*, **11**. 1087, 1107, 1887.

[3] *E.g.*, $CdS.CdCl_2$; $CdS.CdSO_4$—O. Follenius, *Zeit. anal. Chem.*, **13**. 411, 1874.

[4] On evaporating a solution of cadmium sulphate with sulphuric acid, crystals of $CdSO_4.H_2O$ are formed (B. Kühn, *Arch. Pharm.* (2), **50**. 286, 1847; *Schweigger's Journ.*, **60**. 344, 1830; K. von Hauer, *Journ. prakt. Chem.* (1), 64, 477, 1855; (1), **72**. 372, 1857; G. Wyrouboff, *Bull. Soc. Min.*, **11**. 275, 1888; **12**. 366, 1889; F. Mylius and R. Funk, *Ber.*, **30**. 832, 1897; *Zeit. anorg. Chem.*, **13**. 157, 1896; M. de Schulten, *Compt. Rend.*, **107**. 405, 1888). At 100° the water of crystallisation is given off, and anhydrous cadmium sulphate is obtained. Cadmium sulphate can be heated for a long time at a red heat, under the conditions described in the text, without decomposition. At a still higher temperature, the sulphate begins to decompose, first acquiring a yellow tint, and finally passing to a dark brown-coloured oxide. If ammonium chloride be present, ammonium sulphate and cadmium chloride may be formed.

[5] One part of water dissolves 0·59 part of the anhydrous sulphate at 23° (von Hauer).

[6] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 149, 1871; O. Follenius, *Zeit. anal. Chem.*, **13**. 272, 1874; A. Carnot, *Compt. Rend.*, **102**. 621, 1886; *Bull. Soc. Chim.* (2), **46**. 812, 1886; H. Baubigny, *Compt. Rend.*, **142**. 577, 792, 959, 1906.

§ 175. The Volumetric Determination of Cadmium—Berg's Process.

The cadmium may be determined volumetrically, instead of gravimetrically as sulphate, when a standard solution of iodine is available.[1] Collect the precipitated cadmium sulphide on a filter paper or in a Gooch's crucible packed with asbestos. Wash the sulphide with air-free water, and transfer the precipitate by washing with 250 c.c. of air-free water to a 500-c.c. Erlenmeyer's flask. An excess of iodine solution[2] is added along with 10 c.c. of hydrochloric acid (sp. gr. 1·19). The reaction which occurs is represented by the equation:

$$CdS + 2HCl + I_2 = CdCl_2 + 2HI + S.$$

Dilute the solution to about 300 c.c., and titrate the excess of iodine with a standard solution of sodium thiosulphate, as indicated for copper (Haen's process, page 352).

§ 176. The Electrolytic Determination of Cadmium—Beilstein and Jawein's Process.

The electrolytic process for cadmium (page 258) generally gives more accurate results than gravimetric or volumetric processes. The following method is due to Beilstein and Jawein.[3]

The Electrolyte.—Add a drop of phenolphthalein to a solution of a cadmium salt containing, say, 0·5 grm. of the sulphate or acetate. Then add potassium hydroxide until a permanent red colour is obtained. Cadmium hydroxide is precipitated. Add a solution of 98 per cent. potassium cyanide, slowly, with constant stirring, until the precipitate is all redissolved. An excess of the potassium cyanide disturbs the action.[4] Make the solution up to about 150 c.c.

The Electrolysis.—The solution so prepared is electrolysed in the cold[5] with a current density 0·5 to 0·7 amps.,[6] and an electrical pressure of 4·6 to 5 volts.[7] In about 6 hours increase the current density to 1·0–1·2 amps., and continue the electrolysis for about an hour.[8] If the electrolysis is finished, stop the current, wash, dry, and weigh the deposited metal in the usual manner. There is not so much danger of loss by re-solution of the metal when the current is stopped as is the case with copper (page 259).

Preparation of Cadmium Sulphide for Electrolysis.—Cadmium sulphide is usually separated in gravimetric analysis. Dissolve this in nitric acid. Expel the excess of acid by evaporation. Dissolve the dry residue in water, and add potassium hydroxide, etc., as indicated above.

Removal of the Cadmium Deposit from the Electrode.—The removal of cadmium from the cathode presents no particular difficulty. The metal readily dissolves in nitric acid, although it dissolves but slowly in hot hydrochloric and sulphuric acids.

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[1] P. von Berg, *Zeit. anal. Chem.*, **26**. 23, 1887.

[2] Say 7·94 grms. of iodine, and 16 grms. of potassium iodide per litre. One grm. of iodine corresponds with 0·5058 grm. CdO. Hence, 1 c.c. of iodine represents 0·001 grm. of sulphur or 0·004016 grm. CdO.

[3] F. Beilstein and L. Jawein, *Ber.*, **12**. 759, 1879; A. L. Davison, *Journ. Amer. Chem. Soc.*, **27**. 1275, 1905; L. G. Kollock and E. F. Smith, *ib.*, **27**. 1527, 1905.

[4] E. H. Miller and R. W. Page, *School Mines Quart.*, **22**. 391, 1901; *Zeit. anorg. Chem.*, **28**. 233, 1901.

[5] For hot solutions, 50°–60°, a current density of 0·1–0·3 amp. and 3·3–4·5 volts will require between 5 and 6 hours.

[6] The metal is not all precipitated after 12 hours with a current density of 0·5 amp. If 1 amp. be employed at the start, the deposit is non-coherent, and liable to drop off.

[7] If left overnight, use a current density of 0·06 amp. and 3·2 volts.

[8] Test the solution for cadmium by acidifying a few drops with hydrochloric acid; boil to expel the hydrocyanic acid (note, the gas is very poisonous); add a little H_2S water: a yellow precipitate shows that cadmium is still present.

CHAPTER XXVII.

THE DETERMINATION OF ZINC.

§ 177. The Analysis of Silicates containing Zinc Compounds.

If a silicate containing zinc be treated as indicated for clays,[1] several points require special attention.

Silica Evaporation.—It is highly important to remove all the silica during the "evaporation for silica," because, when ammonia is added to a solution containing zinc and silica, in order to remove the iron and alumina,[2] a zinc compound, said to be zinc silicate, will be precipitated. Again, although zinc chloride alone does not volatilise below a red heat, if an acid solution containing zinc and ammonium chlorides be evaporated to dryness, and gradually heated, the chlorides begin to sublime about 145°. Hence, the evaporation of solutions containing silica, zinc, and ammonium chlorides should not be finished at temperatures much higher than 100°.

Ammonia Precipitation.—The addition of ammonia to precipitate iron and aluminium hydroxides leads to the simultaneous precipitation of some zinc hydroxide,[3] and two, better three, reprecipitations are needed to eliminate the zinc from the ammonia precipitate,[4] even when zinc alone is to be determined. For instance, Waring obtained the following results with artificial mixtures of zinc with iron, etc.:—

Table LII.—Contamination of the Ammonia Precipitate by Zinc.

Used.					Zinc found.		
Zinc.	Iron.	NH_4Cl.	Water.	Ammonia solution.	First filtrate.	Second filtrate.	Total zinc.
Per cent.	Per cent.	Grm.	c.c.	c.c.			
60	2	2	33	5	59·10	0·94	60·04
60	2	2	66	5	59·18	0·82	60·00
60	2	2	132	5	59·02	1·03	60·05
60	10	4	66	10	58·87	1·23	60·10
60	10	6	66	10	58·90	1·00	59·90

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[1] Zinc ores are usually decomposed by digestion with acids, say, equal volumes of hydrochloric and nitric acids, and heated on a hot plate until red fumes cease to be evolved. Add 3·5 grms. of ammonium chloride, and heat the solution until it becomes thick and "pasty." When the mass is nearly dry, add 30 c.c. of hot water. If silica be present, filter and wash thoroughly; if an insoluble residue remains, fuse the ignited mass with a little sodium carbonate, take up the cold residue with water, and separate the silica by evaporation to dryness, etc. Add the acid filtrate to the first filtrate.

[2] E. Prost and V. Hassreidter, *Zeit. angew. Chem.*, 5. 166, 1892; W. G. Waring, *Journ. Amer. Chem. Soc.*, 26. 4, 1904.

[3] According to G. Bertrand and M. Savillier (*Bull. Soc. Chim.* (4), 1. 63, 1907), crystals of calcium zincate—$CaH_2Zn_2O_4.4H_2O$—are deposited on boiling an ammoniacal solution of a zinc salt and an excessive proportion of a calcium salt.

[4] W. Funk, *Zeit. angew. Chem.*, 18. 1687, 1905.

In the analysis of three different samples of zinc blende, Waring also obtained[1]:—

Table LIII.—Contamination of the Ammonia Precipitate by Zinc.

Total iron per cent.	Per cent. of zinc.		
	First filtrate.	Second filtrate.	Third filtrate.
8·62	47·20	3·00	0·58
8·75	46·05	4 75	0·40
14·32	16·50	2·05	0·55

It may also be regarded as a general rule *that hydroxides precipitated by ammonia contain silica and phosphates*, unless these substances have been previously removed.

Manganese Precipitation.—If manganese be precipitated, before the zinc, by one of the usual oxidising agents—bromine, hydrogen peroxide, ammonium persulphate, etc.—some zinc hydroxide will be precipitated with the manganese hydroxide.[2] Stone found that manganese oxide precipitated in the presence of bromine from a solution (left after the basic acetate separation) containing 0·2069 grm. of zinc, and 0·2260 grm. of manganese, really contained

Manganese	0·3045	0·2895	0·2840	0·2860	grm.
Zinc	0·1860	0·1780	0·1858	0·1795	grm.

These experiments show that the error is quite serious, particularly if much manganese and little zinc are present. According to Waring, in order to prevent the precipitation of zinc with the manganese, it is necessary to separate the latter as hydrated peroxide, and if the separation be effected from ammoniacal solutions, "the solution should be concentrated and contain a large amount of ammonium chloride."

Precipitation of Zinc as Sulphide.—The zinc can be determined either by the volumetric ferrocyanide process, or precipitated as sulphide. White zinc hydrosulphide is precipitated from neutral solutions of zinc salts by means of hydrogen sulphide,[3] but not if much over 4 c.c. hydrochloric acid (sp. gr. 1·12) be present per 100 c.c. In that case, however, the precipitation can be made if sufficient alkaline acetate, formate, oxalate, etc., be present to form alkaline chloride and set free the organic acid. Many organic acids may be present in considerable quantities without interfering with the precipitation of the sulphide. This is the case, for instance, with formic, acetic, citric, succinic, and chloracetic acids. The theory of the precipitation of zinc sulphide in hydrochloric acid solutions is discussed on page 272;[4] the practice, on page 364.

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[1] According to L. L. de Koninck and E. von Winiwarter (*Bull. Soc. Chim. Belg.*, **26**. 238, 1912) the retention of zinc by ferric oxide is due to the formation of a double hydroxide, and not to adsorption. The retention is prevented by adding 5 per cent. of magnesium (as chloride) and sufficient ammonium chloride to prevent the precipitation of the magnesium hydroxide. E. Beyne, *ib.*, **26**. 355, 1912.

[2] M. Dittrich and C. Hassel, *Ber.*, **35**. 15, 3266, 1902; H. Baubigny, *Compt. Rend.*, **135**. 22, 965, 1902; **136**. 7, 449, 1903; W. G. Waring, *Journ. Amer. Chem. Soc.*, **26**. 4, 1904.

[3] H. Baubigny, *Compt. Rend.*, **107**. 1148, 1888.

[4] According to S. Glixelli (*Zeit. anorg. Chem.*, **55**. 297, 1907), the theory of the action of hydrogen sulphide on zinc salts does not depend upon equilibrium conditions similar to those indicated on page 273. He says that the reaction $ZnSO_4 + H_2S = ZnS + H_2SO_4$ is not reversible, but that a kind of "false equilibrium" occurs in acid solutions which may be very persistent. For the theory of false equilibrium, see J. W. Mellor, *Chemical Statics and Dynamics*, London, 417, 1904. Glixelli's view does not include all the facts.

§ 178. The Theory of the Basic Acetate Separation.

It may now be well to recapitulate our treatment of a complex mixture of colouring oxides with a silicate. The acidified filtrate from the silica was treated with hydrogen sulphide. Lead, bismuth, copper, cadmium, mercury, arsenic, antimony, and tin sulphides were precipitated. The filtrate was boiled to expel the hydrogen sulphide, and treated with an excess of ammonium chloride and ammonia, when aluminium, titanium, and ferric hydroxides were precipitated.[1] Instead of using ammonia as precipitating agent, many prefer the so-called basic acetate separation of iron and aluminium from zinc, manganese, cobalt, and nickel. This separation depends upon the fact that solutions of acetates of iron, aluminium, titanium, chromium, zirconium, and vanadium are decomposed (page 181) when heated, and insoluble sub- or basic acetates are deposited. On the contrary, the acetates of magnesium, manganese, zinc, nickel, and cobalt are stable enough to remain undecomposed when their solutions are boiled for a few minutes.[2]

When sodium carbonate is added to a solution of ferric chloride, the precipitate first formed dissolves in the ferric chloride. One part of ferric chloride will dissolve approximately ten parts of ferric hydroxide.[3] Any further addition of sodium carbonate produces a permanent precipitate, since the ferric chloride is already saturated with the hydroxide. If a solution of ferric chloride, just saturated with the hydroxide, be heated, the mixture decomposes, and ferric hydroxide is precipitated. If sodium or ammonium acetate be added to a solution of ferric hydroxide in ferric chloride, ferric acetate is produced. This is hydrolysed on heating, and a basic ferric acetate is precipitated, while acetic acid passes into solution.

The hydrolysis (page 181) which occurs on boiling is only completed in dilute solutions—at least 500 c.c. of water should be present per gram of ferric hydroxide. For complete precipitation, therefore, as much sodium carbonate should be added as is possible without causing a permanent precipitate; and only sufficient sodium acetate should be added to replace the combined chlorine of the ferric chloride in solution.

If a mixture of aluminium, ferric, nickel, manganese, zinc, and cobalt salts be so treated, the acetates of manganese, zinc, cobalt, and nickel are hydrolysed at a much higher temperature (175°) than the aluminium and ferric acetates. If a large excess of alkaline acetate be present, the acetates of manganese, nickel, cobalt, and zinc are decomposed at a much lower temperature, and they may, in consequence, be precipitated along with the iron and aluminium on boiling the solution. Manganese acetate does not appear to be hydrolysed under these conditions when less than twenty times the required amount of alkaline acetate is present; nickel acetate is more liable to hydrolysis than cobalt; while zinc is next to manganese in its tendency to hydrolyse and form the hydroxide or basic acetate and free acetic acid.[4]

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[1] We ignore *pro tempore* the possible occurrence of certain constituents in both the hydrogen sulphide and in the ammonia groups.

[2] Formates, succinates, and benzoates have been suggested in place of the acetates, but it is generally said that the precipitations are not then so complete (F. Schulze, *Chem. Centr.* (2), **6**. 3, 1861; W. Hisinger, *Afhandlingar i Fysik*, **3**. 153, 1810).

[3] F. Kessler, *Zeit. anal. Chem.*, **11**. 258, 1872; **18**. 8, 1879; *Chem. News*, **27**. 14, 1873.

[4] A. Mittasch, *Zeit. anal. Chem.*, **42**. 492, 1903; W. Funk, *ib.*, **45**. 181, 1906; C. Stöckmann, *ib.*, **16**. 172, 1877; C. Kramer, *ib.*, **16**. 334, 1877; G. Matzurke, *ib.*, **17**. 78, 1878; O. Brunck, *Chem. Ztg.*, **28**. 511, 1904; G. Rosenthal, *Dingler's Journ.*, **225**. 154, 1877; C. Meineke, *Zeit. angew. Chem.*, **1**. 224, 1888; J. Jewett, *Amer. Chem. Journ.*, **1**. 251, 1879; *Chem. News*, **40**. 273, 1879; H. Brearley, *ib.*, **75**. 13, 1897; **76**. 165, 222, 1897; **79**. 193, 1899; A. Jeannel, *ib.*,

Acetic acid is usually added to the solution *before* the alkaline acetate in order to lessen the danger of the joint precipitation of manganese, zinc, cobalt, and nickel along with the aluminium and iron. But since aluminium hydroxide (and phosphate) is soluble in dilute acetic acid, and since alumina usually predominates in silicate analyses, while zinc, nickel, and cobalt, if present at all, only occur in minute quantities, it is best to work with as little free acetic acid as possible when dealing with clays and related substances. The presence of 11 per cent. of acetic acid will prevent the precipitation of the iron, and 5 per cent. will prevent the precipitation of aluminium. In illustration, two solutions containing the equivalent of 0·2 grm. of iron, and 0·2 grm. each of manganese, zinc, nickel, and cobalt, were mixed with 2 grms. of sodium acetate, and each made up to 300 c.c.; 12 c.c. and 3 c.c. of acetic acid (sp. gr. 1·044)—that is, 4 per cent. and 1 per cent. respectively of acetic acid—were added. After treatment by the basic acetate process, the precipitate, according to Brearley, contained the equivalent of

Acetic acid.	Manganese.	Zinc.	Nickel.	Cobalt.
1 per cent. . . .	0·0585	0·2046	0·1770	0·0590
4 per cent. . . .	trace	nil	0·1219	0·0315

The precipitate by the basic acetate process contains titanium, most of the zirconium,[1] vanadium, uranium,[2] as well as phosphorus and arsenic, if present. Chromium (*q.v.*) is precipitated with the iron and aluminium, but the separation is not satisfactory with chromium. This process can also be used for separating iron and aluminium from the rare earths.[3]

The basic acetate process requires careful manipulation when much manganese, nickel, and cobalt are present. A second application of the process is then advisable, by redissolving the precipitate in hydrochloric acid, etc. Moore says four precipitations are necessary, Mackintosh says six! If the process be conducted with due respect for the idiosyncrasies indicated in the text, two acetate precipitations, or one acetate precipitation followed by an ammonia precipitation, will generally suffice. Practical directions for the process now follow.

§ 179. The Basic Acetate Separation.

Neutralisation of the Solution.—Gradually add a concentrated aqueous solution of sodium carbonate from a burette, with constant stirring, until the precipitate begins to disappear slowly;[4] then add a dilute solution in a similar manner until the small precipitate does not disappear with one or two minutes' stirring. If much iron be present, the solution will now have a reddish tint; but if little iron be present, the solution will be almost colourless. Add 3 c.c. of acetic acid (sp. gr. 1·044) to dissolve the precipitate, and allow the solution to stand a couple of minutes.[5] If the solution be not clear, add another drop of dilute acetic acid, and proceed as before. If necessary, repeat the addition of

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17. 286, 1868; T. Moore, *ib.*, **56**. 75, 1887; R. L. Leffler, *ib.*, **77**. 265, 1898; J. B. Mackintosh, *ib.*, **56**. 64, 1887; W. Gibbs, *ib.*, **11**. 102. 1865; *Amer. J. Science* (2), **39**. 58, 1865; W. Herz, *Zeit. anorg. Chem.*, **20**. 16, 1899; B. Reinitzer, *Monats. Chem.*, **3**. 256, 1882; G. Rudorf, *Zeit. phys. Chem.*, **43**. 262, 1903; V. von Eggertz, *Berg. Hütt. Ztg.*, **26**. 187, 1867; W. Hampe, *Zeit. Berg. Hütt. Sal.*, **25**. 253, 1877; F. Mayer, *Ber.*, **22**. 2627, 1889; R. B. Riggs, *Journ. Anal. App. Chem.*, **6**. 94, 1892.

[1] E. Linnemann (*Monats. Chem.*, **6**. 335, 1885) says the separation is not complete. Some zirconium remains with the iron precipitate.

[2] H. Rheineck, *Chem. News*, **24**. 233, 1871.

[3] A. Beringer, *Liebig's Ann.*, **42**. 134, 1842; T. Scheerer, *Pogg. Ann.*, **51**. 467, 1840.

[4] According to H. Tamm (*Chem. News*, **26**. 37, 1872), oxidation with nitric acid leads to the precipitation of manganese with the iron and alumina. It is claimed that the oxidation of the iron is best effected with potassium chlorate.

[5] Some add 3 c.c. of acetic acid (sp. gr. 1·044; that is, 33 per cent.), in excess, for every 100 c.c. of solution in the beaker previous to the dilution. As indicated in the text, an excess of

dilute acetic acid, drop by drop, until the solution does become clear under the conditions stated.

Precipitation.—Dilute the solution to about 400 c.c. and heat to boiling; add about 6 c.c. of sodium acetate solution.[1] Do not boil the mixture more than a minute, or the precipitate will become slimy, and some may dissolve in the acetic acid. The precipitate is bulky and difficult to filter[2] and wash. Filter and wash with hot water containing 50 grms. of sodium acetate per litre.[3] Suck the precipitate dry at the pump. The precipitate is seldom or never ignited and weighed, because it is always contaminated with alkaline salts. Hence, the precipitate must be dissolved in nitric or hydrochloric acid, and reprecipitated with ammonia, as described on page 182.

The process just outlined gives satisfactory results. The presence of sulphates leads to imperfect precipitations.[4] Tartaric, citric, and organic acids should be absent. Indeed, it might here be emphasised that analysts are very chary about introducing organic acids into their solutions, because, if later separations have to be made, there is some uncertainty as to the effect of the organic acids on subsequent precipitations. Tartaric, citric, oxalic, malic, and other organic acids, dextrin, and the sugars, for instance, prevent the precipitation of aluminium, chromium, and ferric hydroxides by ammonia;[5] and of manganese sulphide by ammonium sulphide.[6]

Evaporate the combined filtrates to about 200 c.c. If a precipitate should separate, filter it off, dissolve the precipitate in hydrochloric acid, and precipitate the iron and alumina as basic acetates; add the filtrates to the main filtrate.

Suppose that zinc, cobalt, and nickel be absent, the manganese may now be precipitated by a number of different processes—by bromine, by ammonium sulphide, etc. If cobalt, nickel, or zinc be present, remove the zinc by the formic acid process, and treat the filtrate from the zinc sulphide by the method described below.

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acid, however, leads to an incomplete precipitation of the iron and aluminium; but too little acid will lead to the precipitation of manganese, zinc, nickel, and cobalt, if these elements be present.

[1] SODIUM ACETATE SOLUTION.—Dissolve 167 grms. of sodium acetate in water and make the solution up to 500 c.c. One c.c. of this solution will contain nearly one-third of a gram of sodium acetate. Ammonium acetate is not so suited for the work, although it is sometimes recommended, chiefly because it is removed from the precipitate on ignition. Ammonium acetate has the disadvantage of being more readily hydrolysed (page 181) than sodium acetate in aqueous solution. H. C. Dibbits (*Bull. Soc. Chim.* (2), **18**. 490, 1872; (2), **20**. 258, 1873) says that 7·6 per cent. of ammonium acetate is hydrolysed against 0·14 per cent. of sodium acetate. Hence, on boiling solutions of ammonium acetate ammonia is evolved, and the solution becomes more acid. Hence, the acidity of solutions of ammonium acetate is less easy to control than solutions of sodium acetate. W. Gibbs (*Chem. News*, **11**. 102, 1865) adds the acetate to the cold solution and then heats the solution to boiling. H. Brearley (*ib.*, **79**. 193, 1899) says a large excess of acetate always leads to an imperfect separation of, say, nickel and iron, because (1) the excess of acetate transforms the nickel as well as iron into acetate; and (2) the nickel acetate is partially decomposed along with the ferric acetate. "When the acetate is added to the cold solution, both these factors exert their maximum influence. On adding acetate to the boiling solution, the first portion of it precipitated the iron; when the remaining portion is added, the conditions are changed, for the iron is present in suspension only, and its influence is greatly lessened."

[2] H. N. Warren (*Chem. News*, **61**. 63, 1890) agitates finely powdered glass with the precipitate. He claims that if this is properly done, the glass carries down the precipitate, and enables the washing to be done more quickly. The glass does no harm, since the precipitate is afterwards dissolved in acid.

[3] The filtrate may be tested for iron by potassium ferrocyanide, not thiocyanate.

[4] Sulphates must not be determined in the filtrate from the basic acetate process on account of the great probability of contamination with sulphates by the large amounts of reagents used.

[5] M. Juette, *Compt. Rend.*, **66**. 417, 1868; *Chem. News*, **18**. 63, 1868.

[6] J. Spiller, *Journ. Chem. Soc.*, **10**. 110, 1858; *Chem. News*, **8**. 280, 1863; **19**. 166, 1869; H. How, *ib.*, **19**. 137, 1869; H. N. Draper, *ib.*, **8**. 260, 1863; F. Field, *ib.*, **3**. 65, 1861; F. Pisani, *ib.*, **3**. 257, 1861; L. J. Curtman and H. Dubin, *Journ. Amer. Chem. Soc.*, **34**. 1485, 1912; E. Salkowski, *Zeit. physiol. Chem.*, **83**. 159, 1913.

§ 180. The Separation of Zinc from Manganese, Cobalt, and Nickel.

Assume that the filtrate from the ammonia or basic acetate separation contains zinc,[1] manganese,[2] cobalt, and nickel, as well as magnesia, lime, and the alkalies.

Precipitation of Zinc Sulphide.—The ammoniacal solution is neutralised with formic acid, and about 5 c.c. additional formic acid (sp. gr. 1·2) is added per 150 c.c. of solution. Not more than about 3 per cent. excess of formic acid should be present, or some of the zinc may escape precipitation. Enough sodium formate should be present to react with the inorganic acids set free by the action of the hydrogen sulphide, and so prevent free hydrochloric acid accumulating in the solution.[3] Heat the solution to 50° to 60°. Pass hydrogen sulphide (two bubbles a second) through the warm solution for an hour in order that the zinc sulphide may coagulate, and filter quickly.[4] Zinc sulphide is practically insoluble in formic acid of the strength just indicated; and, like many other sulphides, changes from the colloidal form after precipitation. Hence, it is better to let the mixture stand overnight in a warm place with a slow current of hydrogen sulphide passing through the solution, or else let it stand some time in a corked flask. The larger the excess of formic acid, the slower the separation of the zinc sulphide, and the larger the excess of alkaline acetates or formates present, the more slimy the precipitated sulphide and difficult to filter and wash.

Filtration, and Washing the Zinc Sulphide.—Filter off the precipitated sulphide and test the filtrate with hydrogen sulphide to make sure that all the zinc is precipitated. Wash the precipitate by decantation two or three times with water saturated with hydrogen sulphide, and containing a little formic acid. Collect the washings in separate beakers, so that if the filtrate should commence to run through turbid,[1] as sometimes occurs when the ammonium salts are nearly all washed out, it will not be necessary to re-filter a large quantity of liquid. The precipitate is usually free from manganese, cobalt, and nickel. In case a relatively large amount of these elements be present, the precipitate may be contaminated, and it is advisable to dissolve the precipitate in dilute hydrochloric acid, neutralise with ammonia, and reprecipitate with hydrogen sulphide. Add the second filtrate to the first. The joint filtrates are reserved for the separation of manganese, cobalt, and nickel, as indicated on page 388. The precipitate of zinc sulphide is then treated as indicated in the next section.

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[1] Zinc may be found in reagents kept in Jena and "nonsol" glass bottles page 145. Acids transported in carboys with glass covers secured by zinc rings are liable to contamination owing to the splashing of the acid into the neck of the carboy. This explains how zinc has been reported when no zinc was present in the original sample. A. Vita, *Stahl Eisen*, 32. 1532, 1912; *Sprech.*, 42. 787, 1912.

[2] The manganese may or may not have been removed prior to the zinc.

[3] W. Hampe, *Chem. Ztg.*, 9. 543, 1885; *Chem. News*, 52. 313, 1885; M. Bragard, *Chem. Ztg.*, 10. 729, 1886; E. Dohler, *ib.*, 23. 399, 1899; P. von Berg, *Zeit. anal. Chem.*, 25. 512, 1886; G. Naumann, *ib.*, 28. 57, 1889; W. Funk, *ib.*, 46. 93, 1907; H. Kinder, *Stahl Eisen*, 16. 675, 1896; H. Delffs, *Zeit. Chim. Pharm.*, 4. 1860; *Chem. News*, 41. 279, 1880; T. Cockburn, A. D. Gardiner, and J. W. Black, *Analyst*, 37. 443, 1912. According to Bragard, the solution should have 5 c.c. of formic acid (sp. gr. 1·1136) per 0·03 grm. of nickel in solution, and this amount should not be exceeded if the zinc is to be precipitated completely. If much nickel be present, the solution should be diluted to 500-600 c.c. If the solution be heated, more acid is needed to prevent the precipitation than if the solution be "gassed" cold. A very slight excess of hydrochloric acid added to a neutral solution is sometimes used instead of formic acid, but there is a difficulty in regulating the correct amount of acid, and the results are satisfactory when only small amounts of zinc are present. C. Brunner, *Dingler's Journ.*, 150. 369, 1858; A. Klaye and A. Deus, *Zeit. anal. Chem.*, 10. 190, 1871; F. Oettel, *ib.*, 27. 16, 1888; J. B. Kirkland, *Rep. Australasian Assoc.*, 2. 397, 1890. For acetic acid, see A. Rosenheim and E. Huldschinsky, *Zeit. anorg. Chem.*, 32. 84, 1902; A. Thiel, *ib.*, 33. 1, 1902; H. Nissenson and W. Kettembeil, *Chem. Ztg.*, 29. 950, 1905; J. Flath, *ib.*, 25. 564, 1901; W. G. Waring, *Journ. Amer. Chem. Soc.*, 26. 4, 1904; W. Funk, *Zeit. anal. Chem.*, 46. 104, 1907; M. Bragard, *ib.*, 26. 209, 1887; H. Kinder, *Stahl Eisen*, 16. 675, 1896; J. Platz, *ib.*, 9. 494, 1889; H. Baubigny, *Compt. Rend.*, 108. 236, 450, 1888. For citric acid, see F. Beilstein, *Ber.*, 11. 1715, 1878. For oxalic acid, A. Carnot, *Compt. Rend.*, 102. 678, 1886. For succinic acid, H. Alt and J. Schultze, *Ber.*, 22. 3259, 1889; H. Delffs, *Chem. News*, 41. 279, 1880. For monochloracetic acid, P. von Berg, *Zeit. anal. Chem.*, 25. 512, 1886. For trichloracetic acid, J. J. Fox, *Journ. Chem. Soc.*, 91. 964, 1907. It is claimed that this acid is better for the separation of zinc and cadmium, since the acidity limits are not so narrow as with hydrochloric acid. For benzolmonosulphonic acid, see H. Schilling, *Chem. Ztg.*, 36. 1352, 1912.

[4] Zinc sulphide is a difficult precipitate to filter and wash. It may be gelatinous or in a very finely divided condition suspended in the fluid; in the former case washing is very slow; in the latter case the precipitate passes through the paper (pages 178 and 275). P. Pipereaut and A. A. Vila (*Internat. Cong. App Chem.*, 7. i. 141, 1909) say that zinc sulphide is precipitated in a very dense form, readily washed, by the addition of finely divided sulphur to the boiling alkaline solution. The precipitate is white, and when the precipitation is complete, a pink coloration appears. E. Murmann (*Monats. Chem.*, 19. 404, 1898) adds a little mercuric chloride to the solution before "gassing." The results are good. See page 319.

Influence of Formic Acid.—To illustrate the relation between the amount of acid in the solution and the efficiency of the formic acid separation, the following numbers are quoted from Bragard's work :—

Table LIV.—Effect of Formic Acid on the Separation of Zinc and Nickel as Sulphides.

Zinc. grm.	Nickel. grm.	Volume solution. c.c.	Formic acid. c.c.	Zinc ppd.	Nickel ppd. with zinc per cent.
0·0325	0·0048	300	5	0·0324	54·2
0·0325	0·0048	300	6	0·0325	37·5
0·0325	0·0048	300	7	0·0322	22·9
0·0325	0·0048	300	10	0·0325	0·0
0·0325	0·0096	500	10	0·0325	0·0
0·3252	0·0960	400	10	0.3252	28·1
0·3252	0·0960	500	20	0·3247	18·4
0·3252	0·0960	600	30	0·3252	8·0
0·3252	0·0960	600	40	0·3248	0·0

Manganese, aluminium, cobalt, and iron are not usually precipitated if the solution has 15–20 c.c. of formic acid (sp. gr. 1·2) per 250–500 c.c. of solution ; but if much manganese, etc., are present it is well to make sure that the precipitate is free from contamination, and if necessary a reprecipitation must be made.

The 1904 report of the Committee on Uniformity in Technical Analyses[2] shows analyses of three samples of zinc ore by forty-two chemists. As a result :

	SAMPLE A.		SAMPLE B.		SAMPLE C.	
	Zn.	Fe.	Zn.	Fe.	Zn.	Fe.
Highest results	39·22	21·92	38·86	15·00	59·79	3·26
Lowest results	12·20	18·04	28·90	8·40	56·03	2·10

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[1] O. Mühlhauser, *Zeit. angew. Chem.*, **15**. 731, 1902.

[2] *Journ. Amer. Chem. Soc.*, **26**. 1644, 1904.

The results for samples A and B are surprisingly discordant, and seriously undermine confidence in many published analyses. Each chemist used the particular process he thought best.

§ 181. The Determination of Zinc as Phosphate.

Zinc sulphide is not an easy precipitate to prepare for the balance, and, in consequence, many adopt Tamm's[1] process, in which the zinc is precipitated as phosphate. This is an easy gravimetric process. Although, in practice, with the standard solutions ready made, it is far easier to get good results with the unwashed sulphide by volumetric processes, than by gravimetric methods which involve the washing of the precipitated zinc sulphide.

Dissolve the precipitated sulphide in hot dilute hydrochloric or nitric acid. Boil the solution to expel the hydrogen sulphide. Filter off any sulphur which separates. The acid solution, occupying about 150 or 200 c.c.,[2] is neutralised with ammonia and then made faintly acid with hydrochloric acid. Heat the solution to boiling, add 15 to 20 times as much ammonium phosphate[3] as there is zinc in the solution. If a precipitate does not form, carefully add ammonia until it does.[4] The solution will now be alkaline. Keep the vessel and contents warm on a water bath—10–15 minutes—and the amorphous ammonium zinc phosphate—$ZnNH_4PO_4$—first precipitated will crystallise. If the solution be boiled it bumps badly. Let the precipitate settle.[5] Filter through asbestos[6] in a Gooch's crucible. Clean[7] the beaker with the mother liquid, and wash with hot water containing about 1 per cent. of ammonium phosphate until the precipitate is free from chlorides (silver nitrate with nitric acid is the test). Finish the washing with alcohol. Dry at 100°, and weigh the precipitate as $ZnNH_4PO_4$. This weight, when multiplied by 0·4561, represents the corresponding amount of zinc oxide—ZnO.[8]

The precipitate, if desired, can be ignited to low redness, and weighed as zinc pyrophosphate—$Zn_2P_2O_7$. If the ignition be conducted at too high a temperature, the pyrophosphate may melt, and be absorbed by the asbestos, with but a slight loss in weight—possibly 0·1 per cent. The weight of the pyrophosphate multiplied by 0·53402 gives the corresponding amount of zinc oxide—ZnO.

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[1] H. Tamm, *Chem News*, **24**. 148, 1871; G. Lösekann and T. Mayer, *Chem. Ztg.*, **10**. 729, 1886; L. Jawein, *ib.*, **11**. 347, 1887; M. Bragard, *ib.*, **10**. 1605, 1886; G. C. Stone, *Journ. Amer. Chem. Soc.*, **4**. 26, 1882; R. W. Langley, *ib.*, **31**. 1051, 1909; A. C. Langmuir, *ib.*, **21**. 125, 1899; *Chem. News*, **79**. 183, 1899; H. D. Dakin, *Zeit. anal. Chem.*, **39**. 273, 1900; *Chem. News*, **82**. 101, 1900; M. Austin, *Amer. J. Science* (4), **8**. 206, 1899; R. C. Boyd, *School Mines Quart.*, **11**. 355, 1890; J. Clark, *Journ. Soc. Chem. Ind.*, **15**. 866, 1896; M. Pouget, *Compt. Rend.*, **129**. 45, 1899; K. Voigt, *Zeit. angew. Chem.*, **22**. 2280, 1909; **24**. 2195, 1911; **25**. 205, 1912; V. Hassreidter, *ib.*, **24**. 2491, 1911; **25**. 1005, 1912; K. Voigt, *ib.*, **26**. 47, 1913; Report in *Journ. Ind. Eng. Chem.*, **4**. 467, 1912.

[2] The solution is diluted so as to contain 0·2 to 0·4 grm. zinc per 400 c.c. of solution.

[3] If microcosmic salt be employed, there is more difficulty in washing the precipitate free from alkalies than when the ammonium salt is used.

[4] The precipitate is soluble in acids and ammonia, and slightly soluble in large quantities of ammonium salts. For chromium phosphate, see H. Kämmerer, *Zeit. anal. Chem.*, **12**. 375, 1873.

[5] The important points to observe in precipitation are a large excess of reagent, and sufficient ammonium salts to flocculate the precipitate. If materials other than alkaline salts be present the precipitate may be contaminated accordingly. See the preceding footnote; if too great an excess of ammonium salts be present, a little zinc phosphate may pass into solution.

[6] A slight loss of zinc by reduction to metal, and subsequent volatilisation may occur if filter paper be used and the precipitate be afterwards ignited. If the precipitate be ignited, the asbestos used in the Gooch's crucible should have been previously calcined. Otherwise, drying at 100° will suffice.

[7] The precipitate is inclined to stick tenaciously to the walls of the beaker in which the precipitation is made. It may then be necessary to dissolve the precipitate from the walls with a little acid, evaporate to dryness in a weighed crucible, etc.

[8] Tests made under various conditions show that here less than 0·0003 grm. of zinc phosphate escapes with the filtrate and in the washings.

§ 182. The Volumetric Ferrocyanide Process for Zinc.

Zinc ferrocyanide is precipitated from a hydrochloric acid solution of a zinc salt by potassium ferrocyanide. When all the zinc has been converted into zinc ferrocyanide, any further addition of the potassium ferrocyanide will cause the solution to give a brown coloration with a uranium salt.[1]

Theory of Process.—If the ferrocyanide be gradually added to the solution, there is first a slow formation of normal zinc ferrocyanide:

$$4ZnCl_2 + 2K_4FeCy_6 \rightarrow 8KCl + 2Zn_2FeCy_6.$$

If the solution be cold (20° to 25°), the solution will colour a drop of uranium acetate a fading yellowish brown. When about three-quarters of the required amount of potassium ferrocyanide has been added, the solution no longer affects the indicator—uranium salt. The precipitate becomes flocculent. The slow reaction just indicated is followed by a faster reaction:

$$6Zn_2FeCy_6 + 2K_4FeCy_6 \rightarrow 4K_2Zn_3(FeCy_6)_2.$$

The indicator is coloured permanently when the second reaction is completed. The whole reaction is therefore written:

$$3ZnCl_2 + 2K_4FeCy_6 . 3H_2O \rightarrow Zn_3K_2(FeCy_6)_2 + 6KCl + 3H_2O.$$

After a little practice, the transient colour first produced will not be mistaken for the final permanent coloration. The first coloration gradually fades, and the permanent tint becomes more intense. The solution during the former stage is bluish white, and during the latter stage, pale cream. The first transient coloration of the indicator does not appear if the solutions be hot, because the first reaction proceeds quickly. This reaction is the basis of Galetti's process[2] for the volumetric determination of zinc. If the process be carried out in a regular, uniform manner, comparable and satisfactory results can be obtained. "In my opinion," says Seaman, "the results for zinc by the ferrocyanide process more nearly approach the absolute amount of zinc in an ore than the results obtained by working slowly with the gravimetric process."

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[1] E. H. Miller, *Journ. Amer. Chem. Soc.*, 18. 1100, 1896; 22. 541, 1900; 24. 226, 1902; E. H. Miller and J. A. Matthews, *ib.*, 19. 547, 1897; E. H. Miller and M. J. Falk, *ib.*, 26. 952, 1904; E. H. Miller and J. L. Danziger, *ib.*, 24. 827, 1902; G. C. Stone and D. A. van Ingen, *ib.*, 19. 542, 1897; E. H. Miller and E. J. Hall, *School Mines Quart.*, 21. 267, 1900; *Chem. News*, 82. 177, 1900; F. Reindel, *Dingler's Journ.*, 190. 395, 1868; K. Zulkowsky, *ib.*, 249. 175, 1893; M. Bragard, *Beiträge zur Kenntnis der quantitativen Bestimmung des Zinks*, Berlin, 1887; G. Wyrouboff, *Ann. Chim. Phys.* (5), 8. 444, 1876; L. L. de Koninck and E. Prost, *Zeit. angew. Chem.*, 9. 460, 564, 1896; *Chem. News*, 76. 6, 15, 29, 38, 51, 1897.

[2] M. Galetti, *Zeit. anal. Chem.*, 4. 213, 1865; 8. 135, 1869; 14. 190, 1875; *Bull. Soc. Chim.* (2), 2. 83, 1864; J. Muller, *ib.* (4), 1. 13, 61, 1907; C. Fahlberg, *Zeit. anal. Chem.*, 13. 379, 1874; L. Blum, *ib.*, 29. 271, 1890; 31. 60, 1892; E. Murmann, *ib.*, 45. 174, 1906; *Monats. Chem.*, 19. 404, 1898; L. L. de Koninck and E. Prost (*l.c.*); A. Renard, *Compt. Rend.*, 67. 450, 1868; M. Pouget, *ib.*, 129. 45, 1899; W. G. Waring, *Journ. Amer. Chem. Soc.*, 26. 4, 1904; 29. 265, 1907; A. H. Low, *ib.*, 15. 550, 1893; 22. 198, 1900; W. H. Seaman, *ib.*, 29. 205, 1907; W. H. Keen, *ib.*, 30. 225, 1908; G. C. Stone, *ib.*, 17. 475, 1895; 30. 904, 1908; Reports on this subject, *ib.*, 29. 262, 1907; *Chem. News*, 67. 517, 1893; F. M. Lyte, *ib.*, 31. 222, 1875; W. H. Keen, *ib.*, 98. 201, 1908; *Journ. Amer. Chem. Soc.*, 30. 225, 1908; R. W. Mahon, *Amer. Chem. Journ.*, 4. 53, 1882; H. S. Pattinson and G. C. Redpath, *Journ. Soc. Chem. Ind.*, 24. 228, 1905; E. Donath and G. Hattensauer, *Chem. Ztg.*, 14. 323, 1890; Report in *Chem. News*, 67. 5, 17, 1893; E. Rupp, *Archiv Pharm.*, 241. 331, 1903; E. Rupp, *Chem. Ztg.*, 33. 3, 1909; C. Kirschnick, *ib.*, 31. 960, 1908.

Disturbing Agents.—Anything which oxidises or decomposes the ferrocyanide solution should be absent—strong acids, chlorine, etc. Metals which give insoluble or sparingly soluble ferrocyanides—aluminium, cobalt, cadmium,[1] copper, iron,[2] manganese,[2] lead, nickel, arsenic, antimony, and magnesium—should also be absent. Some of these substances, however, produce no appreciable effect if only present in small quantities—*e.g.*, aluminium and lead.[3]

The composition of the precipitate varies according as the solution is alkaline, neutral, or acid; according as the solution is acid with acetic or hydrochloric acids; if the hydrochloric acid be in excess, the potassium ferrocyanide [4] will be decomposed, forming a blue solution which spoils the work. This all shows that *uniform conditions are indispensable for accurate work.*

The end point is not very sensitive in the presence of hydrochloric acid, but it is sharpened a little in presence of ammonium chloride. In consequence, it is necessary to deduct from the burette reading the amount of the standard ferrocyanide solution in excess of that actually required for the above reaction needed to give the brown coloration with the uranium nitrate used as indicator. Since uranium ferrocyanide is soluble in hydrochloric acid, this excess is dependent upon the amount of hydrochloric acid present. Hence, it is necessary to work under certain definite conditions which experience has shown to be the best, and to determine the allowance to be made for the indicator.

Standardising the Potassium Ferrocyanide Solution.—Dissolve 34·64 grms. of crystalline potassium ferrocyanide—$K_4FeCy_6 . 3H_2O$—in water,[3] and make the solution up to a litre—if not clear, filter.[5] 1 c.c. corresponds with 0·01 grm. of zinc. In order to standardise this solution, ignite pure zinc oxide,[6] and cool in a desiccator to ensure freedom from moisture and carbonates. Dissolve 12·45 grms. in concentrated hydrochloric acid, add ammonia until a slight permanent precipitate is formed; dissolve this in a drop or two of dilute hydrochloric acid; add 30 c.c. of concentrated hydrochloric acid, and 50 grms. of ammonium chloride, and make the solution up to a litre. 1 c.c. corresponds with 0·01245 grm. of ZnO.

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[1] Cadmium salts are fatal to the success of the determination of zinc by the ferrocyanide process. Cadmium ferrocyanides—Cd_2FeCy_6 and $K_2CdFeCy_6$, or a mixture of the two—are formed (E. H. Miller, *Journ. Amer. Chem. Soc.*, **22.** 541, 1900; **24.** 226, 1902). If cadmium, copper, and antimony be present, a difficult separation by hydrogen sulphide may be necessary. It is generally considered best to precipitate the copper, lead, cadmium, and antimony by boiling the dilute hydrochloric acid solution with a piece of metallic aluminium (page 304). If arsenic be present, some iron may escape precipitation with ammonia. In that case, the solution may be evaporated to dryness. Boiling of the residue with concentrated hydrochloric acid and bromine will expel the arsenic. Lead will precipitate copper in an acidified solution. Members of the iron group should be absent. If manganese be present, it can be removed by means of bromine (page 177). A. Renard (*Bull. Soc. Chim.* (2), **11.** 473, 1869) removed manganese by sodium phosphate in ammoniacal solution, and obtained for the analysis of an untreated sample 1·036 grm. zinc; and for the same sample treated previously with sodium phosphate to remove manganese, 0·998 grm. zinc. If copper is to be precipitated with aluminium, ammonium salts should be absent. If much aluminium be present, derived from the solution of metallic aluminium, the results of the ferrocyanide titration will be irregular (E. H. Miller and E. J. Hall, *School Mines Quart.*, **21.** 270, 1900; *Chem. News*, **82.** 177, 1900).

[2] C. Fahlberg (*Zeit. anal. Chem.*, **4.** 213, 1865) removes iron and manganese by shaking the solution with lead dioxide and filtering before titrating.

[3] V. Lehner and C. C. Meloche (*Journ. Amer. Chem. Soc.*, **35.** 134, 1913) show that lead does no harm in the ordinary ferrocyanide titration for zinc.

[4] L. Blum (*Zeit. anal. Chem.*, **24.** 285, 1895) deals with the impurities in commercial potassium ferrocyanide.

[5] F. Moldenhauer (*Chem. Ztg.*, **15.** 223, 1891; *Chem. News*, **64.** 150, 1891) proposes to prevent the decomposition of the solution by adding 1 to 2 grms. of potassium hydroxide per litre. The standard solution should be preserved in darkness.

[6] Zinc oxide is preferable since it is more easily procured free from iron, lead, etc., than metallic zinc.

The Titration.—Pipette 25 c.c. of the standard solution of zinc oxide into a 600 c.c. flask or beaker, and add sufficient water to make about 180–200 c.c. Warm the solution to about 70°–80°, and pour about half into another beaker. Add the standard ferrocyanide solution from a burette, 1 c.c. at a time, until the solution has a greyish colour, and a drop in contact with a drop of uranium nitrate solution[1] on a porcelain plate (page 454) gives a distinct brown coloration. Mix the two solutions. Suppose that 14 c.c. of the ferrocyanide gave no coloration with the first half, and 15 c.c. gave a distinct brown. Then at least 28 c.c. of ferrocyanide solution will be required for the titration. Hence, a total 28 c.c. of ferrocyanide may be added without fear of exceeding the limit. Then add the ferrocyanide drop by drop, and test for the end by means of the spot test. Then pour the solution backwards and forwards from one beaker to the other, and finish the titration. This procedure is less tiresome than titrating the whole solution directly, and there is less danger of exceeding the limit. A little time should be allowed for the spot test to change colour, or the end point may be exceeded. This may be corrected in the following manner:—Let the test drops be added in regular order, and keep a memorandum of the corresponding burette readings. The first drop which shows the brown coloration after standing a short time is the proper reading. This gives the volume of the ferrocyanide solution corresponding with the zinc in the given solution. Hence the amount of zinc oxide is readily computed.[2]

Indicator Allowance.—An allowance should be made for the amount of ferrocyanide in excess of that required to convert all the zinc to ferrocyanide in order to produce the brown coloration with the indicator. Pour 180 to 200 c.c. of water into a beaker, and add 10 grms. of ammonium chloride, 6 c.c. of concentrated hydrochloric acid. Warm the mixture to 70°–80°. Put a number of drops of uranium nitrate on a white tile, and add ferrocyanide from the burette with constant stirring until the solution gives a distinct brown with the indicator. The volume needed should not be greater than 0·5 c.c., and, in subsequent titrations, it should be subtracted, as a correction, from each burette reading.

§ 183. The Evaluation of Zinc Oxide.

When the zinc oxide is to be determined in a commercial sample of the oxide, proceed as indicated in the preceding section for the preparation of standard zinc oxide solution, and keep the conditions as nearly the same as possible: the volume of solution to be titrated, 180–200 c.c.; the solution contains 6 c.c. concentrated hydrochloric acid; 10 grms. ammonium chloride; and the temperature should be between 70° and 80°. A little lead in the solution will not affect the result appreciably.[1]

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[1] Uranium Nitrate Solution.—15 grms. of uranium nitrate in 100 c.c. of water (C. Fahlberg, *Zeit. anal. Chem.*, 4. 213, 1865). H. Nissenson and W. Kettembeil (*Chem. Ztg.*, **20**. 591, 1905) and W. G. Waring (*Journ. Amer. Chem. Soc.*, **26**. 4, 1904) use a 1 per cent. solution of ammonium heptamolybdate instead of uranium nitrate or acetate, provided hydrogen sulphide is absent. A trace of hydrogen sulphide can be destroyed by a small crystal of sodium sulphite. F. Moldenhauer (*Chem. Ztg.*, **13**. 1220, 1889; **15**. 223, 1891; *Chem. News*, **64**. 150, 1891) draws a narrow streak of a 4 per cent. solution of copper sulphate along strips of white filter paper by means of a camel-hair brush. The strips are dried quickly, and preserved in stoppered bottles. When a drop of liquid containing potassium ferrocyanide is placed on the white portion of a strip, if free potassium ferrocyanide soaks into the portion containing copper sulphate a reddish mark is produced. G. C. Stone (*Journ Amer. Chem. Soc.*, **17**. 473, 1895) recommends a dilute solution of cobalt nitrate as indicator, and claims that it gives better results than uranium, copper, and iron salts. Note that commercial "uranium acetate" may be either uranyl acetate or sodium uranyl acetate.

[2] There is a danger of under-titrating when the solution is cold, owing to the slow reaction between the ferrocyanide and the zinc. F. Schulz (*Chem. Ztg.*, **33**. 1187, 1909) places an open tube (12–15 mm. diameter) in the liquid to be titrated, and then titrates as usual; while rotating the beaker, the liquid inside the tube has not been acted upon. Hence, by using the tube as a stirrer, the two liquids mix, and any over-titration is neutralised. The last drops of the standard solution are now added very cautiously.

Zinc oxide is soluble, even after ignition, in a mixture of equal volumes of ammonia (sp. gr. 0·924), solution of ammonium carbonate (20 per cent.), and ammonium chloride (20 per cent.). Hence, Tambon[2] determines the zinc oxide in "zinc white," "grey zinc," etc., by digesting 10 grms. of the sample with 300 c.c. of the above solution and shaking the mixture a few minutes. After standing 10 minutes,[3] filter, wash, and dry the insoluble. The difference between this weight and the original sample represents the zinc oxide. Instead of estimating the soluble zinc by difference, it can be determined volumetrically. If soluble zinc salts are present, they must be first removed by washing with warm water before digesting with Tambon's solution.

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[1] If more hydrochloric acid be employed, the indicator allowance will be larger than 0·5 c.c. and the result will be uncertain.

[2] J. Tambon, *Bull. Soc. Chim.* (4), **I.** 823, 1907.

[3] "Zinc grey" requires 30 minutes' digestion.

CHAPTER XXVIII.

THE DETERMINATION OF MANGANESE.

§ 184. The Effect of Manganese on Silicate Analyses.

FIRECLAYS often contain up to 0·2 per cent. of manganese. This element is usually ignored in clay analyses, and in that case, Hillebrand[1] has shown that manganese, if present, will be found distributed between the ammonia precipitate, the lime, and the magnesia, even when a double ammonia precipitation is made. Much remains in the ammonia precipitate, presumably because the manganese is peroxidised, when it is precipitated in ammoniacal solutions. For instance, Hillebrand found :—

Table LV.—Distribution of Manganese among the Different Constituents of a Clay Analysis.

Composition of rock.			Manganese found.			
Al_2O_3 Fe_2O_3.	CaO.	MgO.	Total.	Al_2O_3 Fe_2O_3 by diff.	CaO.	MgO.
9·35	11·84	2·81	0·311	0·036	0·023	0·252
12·71	11·98	4·30	0·442	0·088	0·016	0·338
4·80	50·51	1·04	0·700	0·301	0·087	0·312
3·49	3·99	0·92	0·016	0·016	nil	nil
1·00	28·04	19·11	0·574	0·032	0·101	0·441

If the manganese is to be determined in a silicate or clay, one of two methods may be adopted.[2] The manganese is either precipitated with the aluminium hydroxide, etc., by peroxidising the manganese as indicated on page 177 ; or the iron and aluminium hydroxides are precipitated by the basic acetate process, redissolved, and reprecipitated by ammonia. The manganese will be found in the combined filtrates.[3] In the former case, the manganese can be determined by the colorimetric process in an aliquot portion of the pyrosulphate fusion. In the latter case, the manganese can be precipitated by ammonium sulphide, or by bromine, and subsequently determined colorimetrically, or gravimetrically as phosphate. The basic acetate process is generally employed for the separation of alumina and iron from manganese, zinc, cobalt, and nickel.

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[1] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **305**. 96, 1907 ; P. de Sorray, *Bull. Assoc. Chim. Sucr. Dist.*, **27**. 671, 1910 ; H. Rose, *Pogg. Ann.*, **110**. 292, 1860 ; *Chem. News*, **2**. 266, 1860.

[2] Of course, a great number of methods are available.

[3] It may be well to bear in mind that laboratory glass generally contains a little manganese, which is dissolved out by alkali—R. A. Gortner, *Amer. Chem. Journ.*, **39**. 157, 1908. This remark is only applicable when minute amounts of manganese are in question.

§ 185. The Precipitation of Manganese by the Bromine Process.

Add 15 c.c. of sodium acetate to the filtrates from, say, the basic acetate separation, and then add 2–3 c.c. of liquid bromine.[1] Heat the solution to boiling. If the solution, on standing, has a yellow colour, sufficient bromine is present; if not, add more bromine. Filter the precipitate through a close-grained filter paper. Add more bromine to the filtrate, and boil again. If more manganese is thrown down, filter, and repeat the process until no manganese is precipitated. Wash the precipitate.[2] If the later washings carry any manganese, re-filter.

The mixed precipitates are now ignited and weighed as Mn_3O_4.[3] This weight multiplied by 0·93007 gives the corresponding amount of MnO. If the crucible be surrounded by oxidising gases during the ignition, the composition of the precipitate will not deviate appreciably from Mn_3O_4; but if reducing gases be present, this formula will not represent the composition of the ignited precipitate (page 184). MnO is formed if the manganese compound be calcined at a red heat in a Rose's crucible (fig. 138) in a vigorous current of hydrogen; and the higher oxides form Mn_3O_4 if ignited in a current of carbon dioxide; and into the sesquioxide, Mn_2O_3, by ignition in a current of oxygen.[4] The MnO formed as just described is said to be a "convenient and accurate form in which to weigh manganese."

The chief disadvantages of the bromine precipitation are: (1) the contamination of the precipitate with alkalies; and (2) uncertainty in the composition of the ignited oxide. A reprecipitation by bromine and ammonia will generally free the precipitate from foreign contaminations. Instead of weighing the precipitate as Mn_3O_4, many prefer to dissolve the moist precipitate in dilute acid and determine the manganese volumetrically; colorimetrically; or gravimetrically by the phosphate process.

Other oxidising agents—ammonium, potassium, or sodium[5] persulphate, hydrogen peroxide, etc.—are often used instead of bromine for precipitating manganese as hydrated peroxide.[1]

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[1] Liquid bromine is recommended because it keeps down the volume of the solution. Some add bromine water, that is, water saturated with bromine. The latter is made by keeping water in a bottle with an excess of liquid bromine. Water at 0° dissolves 4·2 grms. of bromine per 100 c.c.; at 5°, 3·7 grms.; at 10°, 3·4 grms.; at 15°, 3·25 grms.; and at 20°, 2·2 grms. L. L. de Koninck (*Zeit. anal. Chem.*, **18**. 468, 1880; *Chem. News*, **43**. 34, 1881) recommends a saturated solution of bromine in a 10 per cent. aqueous solution of potassium bromide. Others recommend a saturated solution of bromine in concentrated hydrochloric acid. The latter solution is strongly acid; Koninck's solution is neutral. For the presence of bromoform in commercial bromine, see S. Reymann, *Ber.*, **8**. 792, 1877.

[2] It is very difficult to wash the precipitate free from the alkalies carried down by the manganese oxide. Ammonium acetate in place of sodium acetate in the basic acetate separation helps a little, but the separation of manganese is not so good. A. G. M'Kenna, *Tech. Quart.*, **3**. 333, 1890; *Chem. News*, **63**. 184, 1891; V. Eggertz, *ib.*, **18**. 232, 1868; *ib.*, **43**. 226, 1881; C. Reinhardt, *Chem. Ztg.*, **10**. 323, 357, 372, 1896; C. Holthof, *Zeit. anal. Chem.*, **23**. 491, 1884; F. Kessler, *ib.*, **18**. 1, 1879; N. Wolff, *ib.*, **22**. 520, 1883; P. Waage, *ib.*, **10**. 206, 1871; H. Kämmerer, *Ber.*, **4**. 218, 1865.

[3] S. U. Pickering, *Chem. News*, **43**. 225, 1881; C. R. Wright and A. P. Luff, *Journ. Chem. Soc.*, **33**. 525, 1878; W. Dittmar, *ib.*, **17**. 294, 1864; J. and H. S. Pattinson, *Journ. Soc Chem. Ind.*, **10**. 333, 1891; E. H. Saniter, *ib.*, **13**. 112, 1894; H. D. Richmond, *Analyst*, **19**. 99, 1894; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, **17**. 268, 1898; R. Schneider, *Pogg. Ann.*, **107**. 605, 1869; C. Meineke, *Zeit. angew. Chem.*, **1**. 3, 1888; W. C. Heraeus and W. Geibel, *ib.*, **20**. 1892, 1907; A. Gorgeu, *Compt. Rend.*, **106**. 743, 1888; W. W. Randall, *Amer. Chem. Journ.*, **19**. 682, 1897; St C. Deville, *Compt. Rend.*, **56**. 977, 1863; *Chem. News*, **7**. 294, 1863.

[4] P. N. Raikow and P. Tischkoff (*Chem. Ztg.*, **35**. 1013, 1911).

[5] L. Dede, *Chem. Ztg.*, **35**. 1077, 1911.

§ 186. The Precipitation of Manganese by Ammonium Sulphide.

Ammonium sulphide alone precipitates manganese, zinc, nickel, and cobalt sulphides very imperfectly; but if ammonium chloride be present, precipitation is practically complete. Fresenius[2] says that these elements can be precipitated from solution containing the equivalent of $\frac{1}{400,000}$ of manganese oxide, and $\frac{1}{800,000}$ of nickel or cobalt oxides in presence of an excess of ammonium chloride.[3] If free ammonia be present, the precipitation of manganese and nickel sulphides is retarded, and a certain amount of these elements remains in solution.

There are at least two varieties of manganese sulphide. The one is pink or flesh-coloured and colloidal, and readily passes through the filter paper. Nor does the pink variety settle readily from the solution. The other sulphide is green in colour, coarse grained, crystalline, and settles quickly. The latter can be easily filtered and washed. The pink variety, in presence of an excess of ammonium sulphide,[4] soon passes into the green variety when heated, but the change is retarded by the presence of ammonium chloride. Hence, ammonium chloride facilitates the separation of manganese sulphide, but hinders the transformation of the pink into the green sulphide. The pink modification is the first product of the reaction, and this is transformed into the green modification later on. The analyst must therefore employ methods which ensure a complete conversion of the manganese into sulphide, and the transformation of the pink into the green sulphide. The best conditions are: (1) a large excess of ammonium chloride; and (2) a large excess of ammonium sulphide in hot solutions. The ammonium sulphide must be free from yellow polysulphide, since manganese sulphide is slightly soluble in ammonium polysulphide.[5]

Suppose, then, that the manganese is to be precipitated by ammonium sulphide. Evaporate the filtrate, as indicated above, to about 200 c.c. Pour the solution into an Erlenmeyer's flask; add 10 c.c. of ammonium chloride solution, and ammonia until the solution is alkaline. Pass hydrogen sulphide through the boiling solution[6] for about 10 minutes. Cork the flask and let it stand for about 24 hours in a warm place.[7] This procedure gives a granular precipitate.[1] Collect the precipitate[2] on a small filter paper—say 7·5 cm. diameter. Wash with water containing a little colourless ammonium sulphide.[3] Dissolve the precipitate in a little dilute sulphuric acid if the manganese is to be determined colorimetrically, or in hydrochloric acid if the manganese be determined gravimetrically as phosphate.

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[1] M. Dittrich and C. Hassel, *Ber.*, **36.** 284, 1423, 1903; *Zeit. anal. Chem.*, **43.** 382, 1904; M. Dittrich, *Ber.*, **35.** 4072, 1902; M. E. Pozzi-Escot, *Ann. Chim. Anal.*, **7.** 376, 1902; H. Baubigny, *Compt. Rend.*, **135.** 965, 1110, 1902; **136.** 449, 1325, 1903; J. von Knorre, *Zeit. angew. Chem.*, **14.** 1149, 1901; **16.** 905, 1903; *Zeit. anal. Chem.*, **43.** 1, 1904: **44.** 88, 1905; E. Donath, *ib.*, **44.** 698, 1905; H. Lüdert, *Zeit. angew. Chem.*, **17.** 422, 1904; H. P. Smith, *Chem. News*, **90.** 237, 1904; H. Rubricus, *Stahl Eisen*, **25.** 890, 1905.

[2] R. Fresenius, *Journ. prakt. Chem* (1), **82.** 265, 1861; *Zeit. anal. Chem.*, **11.** 419, 1872; H. Raab and L. Wessely, *ib.*, **42.** 433, 1903; A. Classen, *ib.*, **16.** 319, 1877; **8.** 370, 1869; C. Meineke, *Zeit. angew. Chem.*, **1.** 3, 1888; A. Völker, *Liebig's Ann.*, **59.** 38, 1846; P. de Clermont and H. Guiot, *Bull. Soc. Chim.* (2), **27.** 353, 1877; J. C. Olsen and W. S. Rapalje, *Journ. Amer. Chem. Soc.*, **26.** 1615, 1904; J. C Olsen, E. S. Clowes, and W. O. Weidmann, *ib.*, **26.** 1622, 1904; F. Muck, *Zeit. Chem.* (2), **5.** 580, 1869; (2), **6.** 6, 1870; H. How, *Chem. News*, **19.** 137, 1870; W. Böttger, *Ber.*, **33.** 1019, 1900; *Chem. News*, **82.** 247, 1900.

[3] And $\frac{1}{800,000}$ of zinc oxide, if zinc be present.

[4] Not with sodium or potassium sulphides (Muck, *l.e.*).

[5] For the retarding action of salts of organic acids on the precipitation of manganese sulphide, see page 363; and for the retarding action of ammonium salts, see H. Rose, *Chem. News*, **2.** 302, 1860.

[6] E. Murmann (*Monats. Chem.*, **19.** 404, 1898) adds a little mercuric chloride before passing the hydrogen sulphide through the hot solution. The precipitate of the green sulphide so obtained is easily filtered and washed. The mercury, of course, volatilises as soon as the precipitate is ignited.

[7] If the solution happens to contain much lime, as sometimes occurs in the analysis of blast-furnace slags, the prolonged standing leads to the formation of crystals, probably calcium thiosulphate (L. Blum, *Zeit. anal. Chem.*, **28.** 454, 1889). In that case, it is better to follow

§ 187. The Gravimetric Determination of Manganese—Gibb's Phosphate Process.

Manganese is separated from the alkaline earths by precipitation with bromine, or ammonium sulphide, etc. The precipitate is dissolved in hydrochloric acid (1 : 1), and alkaline phosphate is added to the solution. A precipitate of ammonium manganese phosphate is obtained similar to the precipitate obtained with magnesium.[4] This is converted into the pyrophosphate by ignition and then weighed.

First Precipitation.—The cold solution of the manganese oxide in hydrochloric acid (1 : 1) is supposed to contain no more manganese than is represented by 0·1 grm. MnO per 100 c.c. of solution. Add an excess, say 5 c.c., of a cold saturated solution of microcosmic salt[5] with constant stirring. Then add a slight excess of dilute ammonia. Heat the mixture until the precipitate becomes crystalline, and let the whole stand for about 1½ hours, till cold. Filter and wash with cold, slightly ammoniacal water, dry the precipitate at a gentle heat, and ignite as described below. If the manganese salt is associated with other salts in solution, a second precipitation may be made. A large excess of microcosmic salt is necessary in order to render the precipitate insoluble, especially in the presence of ammonium salts.[6]

H. Rose (*Ausführliches Handbuch der analytischen Chemie*, Braunschweig, 1. 167, 1864) and boil the solution while adding ammonium sulphide again and again. Filter at once. No calcium thiosulphate is then formed.

[1] A black residue indicates that manganese, zinc, nickel, cobalt, copper, or platinum may be present. With clays, however, there is little chance of this, but platinum may be derived from the platinum crucible during the pyrosulphate fusions. For the separation when zinc, etc., is present, see page 364.

[2] If some sulphide sticks to the walls of the flask or beaker, wash the vessel with dilute nitric acid. The resulting solution is either added to that obtained by dissolving the precipitate, or it is evaporated to dryness in a weighed crucible, calcined to Mn_3O_4, and the result added to the weight of the main precipitate. It is important to test the filtrate for manganese, and to test the precipitate for silica, barium, etc., if only one precipitation followed by roasting to Mn_3O_4 be made—J. and H. S. Pattinson, *Chem. News*, 81. 193, 1900.

[3] L. Blum (*Zeit. anal. Chem.*, 44. 7, 1905) says there is frequently a slight oxidation of sulphide to sulphate, and in consequence traces of barium and strontium sulphates, if present, may be precipitated.

[4] W. Gibbs, *Chem. News*, 17. 195, 1868 ; *Amer. J. Science* (2), 44. 216, 1867 ; *Zeit. anal. Chem.*, 7. 101, 1868 ; R. Fresenius, *ib.*, 11. 415, 1872 ; F. Kessler, *ib.*, 18. 8, 1879 ; H. D. Dakin, *ib.*, 39. 784, 1890 ; *Chem. News*, 83. 37, 1900 ; W. Böttger, *ib.*, 82. 101, 1900 ; *Ber.*, 33. 1019, 1900 ; A. G. M'Kenna, *Tech. Quart.*, 3. 333, 1890 ; *Chem. News*, 63. 184, 1891 ; T. Moore, *ib.*, 63. 66, 1891 ; G. L. Norris, *Journ. Soc. Chem. Ind.*, 20. 551, 1901 ; E. H. Saniter, *ib.*, 13. 112, 1894 ; R. C. Boyd, *School Mines Quart.*, 11. 355, 1890 ; L. Rürup, *Chem. Ztg.*, 20. 285, 337, 1896 ; A. Ledebur, *ib.*, 8. 910, 927, 963, 1884 ; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, 18. 339, 1898 ; *Amer. J. Science* (4), 6. 233, 1898 ; *Chem. News*, 78. 239, 246, 1898 ; C. E. Munroe, *Amer. Chem.*, 7. 287, 1877.

[5] AMMONIUM SODIUM PHOSPHATE SOLUTION.—A saturated solution has nearly 170 grms. per litre. 1·5 grms. suffice for 0·1 grm. of MnO. Hence 9 c.c. will be required per 0·1 grm. MnO.

[6] The proportion of ammonium chloride to the ammonium manganese phosphate should be as 50 : 1. A very large excess of ammonium chloride may be added without any perceptible solvent action. R. Fresenius (*l.c.*) says that 1 part of the precipitate dissolves in 32,092 parts of cold water, in 20,122 parts of boiling water, and in 1775 parts of a solution of ammonium chloride (1 : 70). This latter statement, however, does not hold good when an excess of the phosphate used for precipitating is present.

Second Precipitation.—Redissolve the precipitate in an excess of sulphuric or hydrochloric acid. Heat the solution to boiling and add a slight excess of ammonia and microcosmic salt solution. The flocculent white gelatinous precipitate of manganese ammonium phosphate so produced passes into a flesh-coloured crystalline precipitate—NH_4MnPO_4—when the solution is boiled, or allowed to stand for some time.[1] The precipitation is best performed in a platinum vessel; but a glass vessel is quite satisfactory. When cold, filter either through an asbestos-packed Gooch's crucible or through filter paper, and wash with cold water or, better, very dilute ammonia until the wash-water acidified with nitric acid gives no turbidity with a drop of silver nitrate solution. This is important.[2] Add more microcosmic salt to the filtrate. If a precipitate settles after standing several hours, filter it through a small filter paper. Dry the precipitates.

Ignition of the Precipitate.—If the filtration has been done through filter paper, transfer the dry precipitate to a watch-glass. Ignite the paper separately in a porcelain crucible. Then transfer the precipitate from the watch-glass, and ignite at a red heat. The temperature should be raised very gradually, in order to prevent any solid from being carried away with the ammoniacal vapours. The ignited precipitate should be white or pale pink.

Calculation.—The weight of the calcined manganese pyrophosphate—$Mn_2P_2O_7$—multiplied by 0·5 (or, more exactly, by 0·4998), and divided by the weight of the sample, represents the amount of manganese oxide—MnO—in the given sample.

Errors.—If the precipitate be coloured brown, the manganese was not all converted into the phosphate. In that case, redissolve the precipitate in hydrochloric acid (1 : 1), and repeat the precipitation with more microcosmic salt. If the precipitate is not all soluble in the hydrochloric acid, some silica was probably precipitated with the manganese. In that case, filter the solution, wash, ignite, and weigh the insoluble silica. Deduct the weight of the silica from the weight of the manganese phosphate.

The process does not give good results in the presence of zinc, nickel, copper, and other metals which give precipitates of sparingly soluble phosphates in ammoniacal solutions. It is an excellent method for converting precipitates by bromine, etc., into a weighable form, and for separating manganese from the elements which are not liable to precipitation in ammoniacal phosphate solutions.

Gooch and Austin found, in using 50 c.c. of a saturated solution of microcosmic salt, 20 grms. of ammonium chloride, and a solution diluted to 200 c.c. containing :

MnO used . . .	0·0942	0·0942	0·0942	0·1885	0·1885	0·1885	grm.
MnO found . . .	0·0951	0·0955	0·0956	0·1888	0·1886	0·1889	grm.
Error	0·0009	0·0013	0 0014	0·0003	0·0001	0·0004	grm.

The positive error here observed appears to be due to the slight adsorption of the microcosmic salt by the precipitated phosphate. The average error in duplicate determinations did not, therefore, exceed 0·001 grm. when expressed in terms of MnO.

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[1] A large excess of ammonium chloride favours a rapid transformation ; ammonium nitrate is not so good.

[2] Ammonium chloride would, of course, be volatilised during the ignition, but a trace of manganese chloride might be formed. There is no danger from this if the washing be conducted as described in the text.

§ 188. The Volumetric Determination of Manganese—Pattinson's Process.

A large number of rapid methods have been suggested, by precipitating the manganese as hydrated manganese dioxide—possibly $MnO(OH)_2$—by potassium chlorate;[1] zinc oxide and bromine;[2] bleaching powder and ferric chloride;[3] etc., and subsequently determining the manganese dioxide by one of the many available volumetric processes. These processes can be made to give accurate results under special conditions, but there is some uncertainty as to the composition of the precipitate, and in routine work an allowance is frequently made for the deviation in the composition of the precipitate from the assumed $MnO(OH)_2$. When ores are only occasionally analysed, the corrections are troublesome. Ledebur, Saniter, Rürup, and others have examined Volhard's, Pattinson's, and other methods. Pattinson's gives excellent results. This process is based on the fact that the whole of the manganese in a solution of manganese chloride can be precipitated as manganese dioxide in the presence of ferric or zinc chloride by an excess of an aqueous solution of calcium hypochlorite, or bromine water.

Dissolution of the Mineral.—Digest 10 grms. of the finely powdered and dried (110°) mineral in 100 c.c. of concentrated hydrochloric acid. Add 5 c.c. of nitric acid, and evaporate down to a small volume.[4] Transfer the solution to a 100-c.c. flask and make up to the mark with water.

Conversion of the Manganese Chloride into Manganese Peroxide.—Agitate the contents of the flask, and pipette 20 c.c. into a litre beaker or Erlenmeyer's flask.[5] Add granular precipitated calcium carbonate, in small quantities at a time, until the free acid is neutralised, and the solution, though clear, has a reddish-brown tinge. Then add 30 c.c. of a solution of zinc chloride,[6] and 50 c.c. of a solution[7] of "chloride of lime" (or 25 c.c. of a saturated aqueous solution of bromine). Add more calcium carbonate, with constant stirring, until the latter remains undissolved. Now stir in 700 c.c. of hot water at about 70°. The supernatant liquid should be colourless. If it be pink (calcium permanganate), add 2 c.c. methyl alcohol and boil; if it still be pink, repeat the treatment with methyl alcohol. Let the precipitate settle. Decant the clear supernatant liquid through an asbestos-packed Gooch's crucible.[1] Wash four times by decantation with 300 c.c. of hot water (70°). Transfer the precipitate to the Gooch's crucible without attempting to remove the last portions of the precipitate from the sides of the beaker. Wash the precipitate with hot (70°) water until the filtrate gives no blue coloration with starch paper.

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[1] W. Hampe and M. Ukena, *Zeit. anal. Chem.*, **24**. 431, 1885; **32**. 369, 1893; A. P. Ford, *Trans. Amer. Inst. Min. Eng.*, **9**. 397, 1880; F. Williams, *ib.*, **10**. 100, 1881; R. Bolling, *Journ. Amer. Chem. Soc.*, **23**. 493, 1901.

[2] A. H. Low, *Journ. Anal. App. Chem.*, **6**. 663, 1892; *Chem. News*, **67**. 162, 1893.

[3] J. Pattinson, *Journ. Chem. Soc.*, **35**. 365, 1879; *Journ. Soc. Chem. Ind.*, **5**. 422, 1886; J. and H. S. Pattinson, *ib.*, **10**. 333, 1891; R. W. Atkinson, *ib.*, **5**. 365, 1886; E. H. Saniter, *ib.*, **13**. 112, 1894; J. Pattinson, *Chem. News*, **21**. 267, 1870; **41**. 179, 1880; G. Lunge, *ib.*, **41**. 78, 120, 141, 179, 181, 1880; W. Weldon, **41**. 207, 1880; C. R. Wright, *Journ. Chem. Soc.*, **37**. 22, 49, 1880; A. Ledebur, *Chem. Ztg.*, **8**. 910, 927, 963, 1884; F. Jean, *Bull. Soc. Chim.*, (3), **9**. 248, 1895.

[4] The insoluble residue may be filtered off, ignited, and fused with sodium carbonate, and if it be coloured greenish blue, take up the melt with water and dilute hydrochloric acid and add it to the main solution.

[5] Add sufficient ferric chloride to make the amount of ferric and manganese chlorides present in the solution approximately equal. This ensures the precipitation of manganese dioxide instead of some lower oxide.

[6] Containing the equivalent of half a gram of metallic zinc per 30 c.c. If ferric chloride be used in place of zinc chloride, an error amounting to 0·4–0·5 per cent. of manganese may be introduced into the determination owing to the presence of manganese in this salt. To correct, the amount of manganese in the ferric chloride can be determined by boiling the solution with ammonia and a little hydrogen peroxide, washing the precipitate in nitric acid and a little sulphurous acid, and determining the manganese by the colorimetric process.

[7] Mix 15 grms. of fresh bleaching powder with 100 c.c. of water, and, after standing some time to settle, decant the clear.

The Titration.—The precipitate and the asbestos are placed in the original beaker. Dissolve the precipitate in dilute sulphuric acid (1 : 1). When the brown colour has disappeared,[2] add 50 c.c. of a freshly standardised solution of ferrous sulphate[3] acidified with sulphuric acid. Mix the solution thoroughly, and then titrate the excess of ferrous sulphate[4] with $\frac{1}{10}$N-potassium dichromate solution.[5]

Calculations.—Ten grms. of the ore were dissolved in 100 c.c. of solution, and 20 c.c., equivalent to 2 grms. of the ore, were taken. 50 c.c. or 3·5 grms. of ferrous ammonium sulphate solution, representing 89·24 c.c. of the $\frac{1}{10}$N-dichromate, were added; but only 38·4 c.c. of the dichromate solution were required in the titration. Hence, 2 grms. of the ore represented 50·84 c.c. of the dichromate solution. But 1 c.c. of $\frac{1}{10}$N-dichromate solution represents 0·004347 grm. of MnO_2 (or 0·003547 grm. MnO); hence, 50·84 c.c. of the dichromate solution represents 0·221 grm. MnO_2 (or 0·180 grm. MnO). That is, 2 grms. of the ore has the equivalent of 0·221 grm. MnO_2 (or 0·180 grm. MnO); that is, 0·11 per cent. of MnO_2 (or 0·09 per cent. MnO).

Errors.—This method will give results within 0·1 per cent. of the true percentage of manganese in a given sample. Lead, copper, nickel, cobalt, and chromium lead to high results. The interference of up to 1 per cent. of lead, copper, and nickel is not serious, but cobalt and chromium spoil the results. Higher oxides of these elements are probably precipitated with the manganese dioxide, and, later on, oxidise the ferrous sulphate. For instance, 100 parts of Mn_3O_4, with 1 part of the elements indicated, gave the following results:

Lead.	Copper.	Nickel.	Cobalt.	Chromium.	
100·23	100·23	100·23	100·64	100·60	per cent.

In the absence of these disturbing elements, 100 ± 0·1 per cent. would have been obtained.

§ 189. The Volumetric Determination of Manganese—Volhard's Process.

Guyard[6] has shown that if a feebly acid or neutral solution of manganese sulphate or nitrate be treated with a solution of potassium permanganate, a compact dark brown precipitate of a manganic acid is formed, which is sometimes said to be H_2MnO_3. The permanganate is decolorised as long as any manganese salt remains in solution; any further addition of the permanganate produces a pink coloration. In reality, the manganic acid $MnO(OH)_2$ is not precipitated, but rather a manganese manganite whose composition varies with the conditions of the experiment. It is accordingly difficult to get uniformly good results with Guyard's process. The reaction has been the subject of many investigations.[1] Volhard showed that the process is more under control, for analytical purposes, if a strongly basic oxide be present in the solution. Mercury, calcium, magnesium, barium, and zinc salts may be used, but the latter appears to be most suitable. Meineke considered that a considerable amount of zinc sulphate —25–30 grms.—is needed for the purpose. The titration can be conducted with a greater degree of precision in the presence of some zinc sulphate, and the consumption of permanganate then corresponds with:

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[1] The asbestos should be tested by a blank experiment with ferrous sulphate to make sure that it contains nothing which will reduce the manganese dioxide. G. W. Sargent and J. K. Faust (*Journ. Amer. Chem. Soc.*, **21**. 287, 1898) use a filter tube packed first with glass-wool, then with sand, and finally with asbestos.

[2] If the ore contains organic matter, this must be filtered off before attempting to oxidise the ferrous salt, since organic matter will reduce the ferric salts and give a high result. Or the solution may be filtered through a Gooch's crucible and the subsequent titrations made with permanganate instead of the dichromate, as indicated in the text.

[3] Containing the equivalent of about 10 grms. of metallic iron per litre; *i.e.* 70 grms. of ferrous ammonium sulphate per litre.

[4] A. Terreil, *Bull. Soc. Chim.* (2), **35**. 551, 1881.

[5] In any case the dichromate or permanganate used for the titration should be standardised with zinc or ferric chloride equal to the amount used in the determination.

[6] A. Guyard, *Chem. News*, **8**. 292, 1863; *Zeit. anal. Chem.*, **3**. 373, 1864; *Bull. Soc. Chim.* (2), **6**. 88, 1863; F. Jean, *ib.* (3), **9**. 248, 1893.

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Ferrous salts should be absent, since they are transformed by the permanganate into ferric salts. Bromine, hydrogen peroxide, etc., can be used to oxidise the iron, but the excess of the oxidising agent must be removed by boiling. If ferric salts be present, they can be precipitated by the addition of zinc oxide, or by sodium bicarbonate, as in Särnström's method. It is somewhat difficult to see when the reaction is complete, because the manganic oxide suspended in the liquid masks the rose colour of the permanganate. The precipitate, however, coagulates on warming, and then settles quickly. Volhard's process, more or less modified, is as follows:—

Dissolution of the Manganese.—Dissolve a gram of the sample in a porcelain basin with a suitable acid, say, 10 c.c. of concentrated hydrochloric acid,[2] assisted, if necessary, by nitric acid,[3] particularly if sulphides be present, and ferrous iron is to be oxidised. Add 10 c.c. of concentrated sulphuric acid, and heat the mixture until the sulphuric acid fumes copiously.[4] When cold, add 25 c.c. of water, and boil the solution a short time to dissolve the ferric sulphate. Transfer the mixture to a 500-c.c. flask.

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[1] J. Volhard, *Liebig's Ann.*, **198.** 218, 1879; *Chem. News*, **40.** 207, 1879; F. W. Daw, *ib.*, **79.** 25, 1899; T. Morawski and J. Stingl, *ib.*, **38.** 297, 1878; *Journ. prakt. Chem.* (2), **18.** 96, 1878; A. Ghilian, *Rev. Univ. Mines* (3), **3.** 270, 1888; *Chem. News*, **59.** 121, 1889; E. Donath, *ib.*, **43.** 253, 1881; F. W. Daw, *ib.*, **79.** 25, 58, 1899; H. Brearley, *ib.*, **79.** 47, 83, 1899; L. Kürup, *Chem. Ztg.*, **15.** 149, 1891; A. Ledebur, *ib.*, **12.** 927, 1888; **8.** 829, 1884; W. Hampe, *ib.*, **7.** 1104, 1883; E. Dliss, *ib.*, **34.** 237, 1910; E Donath, *ib.*, **34.** 437, 1910; A. Kaysser, *ib.*, **34.** 1225, 1910; R. Schöffel and E. Donath, *Oester. Zeit. Berg. Hütt.*, **31.** 229; 1883; C. G. Särnström, *Berg. Hütt. Ztg.*, **40.** 425, 1881; *Zeit. anal. Chem.*, **22.** 84, 1883; L. Blum, *ib.*, **30.** 210, 1891; M. Orthey, *ib.*, **47.** 547, 1908; L. Karaoglanoff, *ib.*, **49.** 419, 1910; C. Winkler, *ib.*, **3.** 423, 1864; R. Habich, *ib.*, **3.** 474, 1864; W. M. Fischer, *ib.*, **48.** 751, 1909; N. Wolff, *ib.*, **43.** 564, 1904; *Stahl Eisen*, **4.** 702, 1884; C. Reinhardt, *ib.*, **5.** 782, 1885; **6.** 150, 1886; C. Meineke, *Zeit. anal. Chem.*, **24.** 423, 1885; *Rep. anal. Chem.*, **3.** 337, 1883; **5.** 1, 1885; *Zeit. angew. Chem.*, **1.** 228, 1888; E. W. Mayer, *ib.*, **20.** 1980, 1907; A. Longi and S. Camilla, *Gaz. Chim. Ital.*, **27.** 87, 1897; G. C. Stone, *Journ. Amer. Chem. Soc.*, **18.** 228, 1896; W. S. Thomas, *ib.*, **17.** 341, 1895; W. A. Noyes, *ib.*, **24.** 243, 1902; G. Auchy, *ib.*, **17.** 943, 1895; **18.** 498, 1896; C. T. Mixer and H. W. du Bois, *ib.*, **18.** 385, 1896; E. Cahen and H. F. V. Little, *Analyst*, **36.** 52, 1911; W. Heike, *Stahl Eisen*, **29.** 1921, 1909; E. Müller and P. Koppe, *Zeit. anorg. Chem.*, **68.** 160, 1910; P. Slawik, *Chem. Ztg.*, **36.** 106, 1912; L. Karaoglanoff, *Jahrb. Univ. Sofia*, 33, 1911.

[2] Chlorides, over 0·5 grm. per litre, should be absent, or the results will be high. If chlorides be present, the precipitate may have a reddish colour; if absent, dark brown. Evaporation with sulphuric acid until the acid fumes copiously will drive off the combined chlorine.

[3] If the manganese is to be determined in the insoluble residue, fuse the insoluble matter with sodium carbonate, dissolve the resulting mass in acid, and add the result to the main solution.

[4] Organic matter should be absent. It can be destroyed by calcination, or evaporation of the solution to dryness with sulphuric acid, or with nitric acid followed by calcination.

Precipitation of Iron.—Nearly neutralise the solution with sodium carbonate, and, if iron be present, add gradually an emulsion of zinc oxide[1] in slight excess. Shake the mixture well after each addition, and avoid a large excess of the zinc oxide. Fill about three-fourths of the flask with water. Agitate the contents of the flask,[2] and let the mixture stand to allow the ferric oxide to settle. If the solution be not colourless, more zinc oxide is probably needed. Make the solution up to the mark with distilled water. Agitate the solution, and let the matter in suspension settle.

The Titration.—Pipette 100 c.c. of the clear supernatant liquid into a 250-c.c. flask.[3] Heat the solution, and titrate, while hot, with a standard solution of potassium permanganate. The permanganate produces a precipitate which discolours the liquid, and it is necessary to titrate cautiously by agitating the flask after each addition, and allowing the precipitate to settle sufficiently after each addition to show whether or not the liquid is coloured pink.[4] The colour is best observed by holding the flask against a white background, and observing whether or not the upper edges of the liquid are coloured pink. Warm the solution to be titrated, but the liquid must not be boiled.[5] If the pink colour fades, add more permanganate. When the pink colour is permanent, take a final reading of the burette.

Calculations.—The permanganate is prepared by the method employed on page 193. On comparing the equation on page 198 for ferrous salts with that indicated above, page 378,[6] it will be observed that, in the case of iron, $2KMnO_4$ represent $5Fe_2O_3$; and here, $2KMnO_4$ represent $3MnO$. Consequently, $3MnO$ correspond with $5Fe_2O_3$. Hence, 1 grm. of Fe_2O_3 corresponds with 0·2665 grm. of MnO.[7]

Errors.—A comparison of the results with the three processes here indicated on a commercial sample of "manganese oxide" gave :

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[1] ZINC OXIDE EMULSION.—A mixture of pure zinc oxide and water will generally do the work—"generally," because some samples of commercial zinc oxide are not effective in separating iron from manganese, possibly owing to the crystalline structure of the powder. A better emulsion is made by dissolving zinc chloride in water; or by dissolving zinc oxide in hydrochloric acid, heating the mixture with a little bromine, and filtering off the excess of zinc oxide. Precipitate zinc hydroxide from the solution by the addition of ammonia. Do not add an excess of ammonia, or the zinc hydroxide will dissolve. Wash the precipitate several times by decantation with hot water, and wash the oxide into a bottle, which is stoppered and preserved. Shake the mixture well before use. F. A. Emmerton, *Trans. Amer. Inst. Min. Eng.*, **10.** 201, 1881. A. Guyard (*Compt. Rend.*, **97.** 673, 1883 ; *Chem. News*, **48.** 193, 1883) reports the presence of manganese in zinc oxide. L. L. de Koninck tests the suitability of the zinc oxide for the determination by triturating 3 grms. with 30 c.c. of water containing 1 grm. of iron alum in solution. The mixture is agitated with sufficient 6N-sulphuric acid to dissolve all the zinc oxide. Avoid a large excess of acid. One drop of the permanganate solution should give a permanent pink coloration. If not, metallic zinc or zinc sulphide may be present.

[2] Many here recommend the addition of a couple of drops of nitric acid.

[3] The precipitate in the flask may appear bulky, but, as a matter of fact, it occupies very little volume. See page 73 for a discussion on the volume of suspended precipitates. The error is here negligible.

[4] It sometimes saves time to take two aliquot portions. Titrate one by adding 1 c.c. of the permanganate at a time, and in the other the titration can be carried to a greater precision without an inordinate expenditure of time.

[5] Owing to the well-known instability of the permanganate in the presence of the solid manganese oxide (page 196).

[6] See J. W. Mellor, *Modern Inorganic Chemistry*, London, 480, 1912.

[7] Some workers deduct 0·2 c.c. from the volume of permanganate employed in the titration before the calculation is made, in order to allow for the presence of the two drops of nitric acid which is supposed to facilitate settling and to counteract the effect of traces of organic matter.

Gibb's phosphate process	74·84	74·85	74·80	per cent. MnO.
Volhard's process	74·68	74·66	74·56	per cent. MnO.
Pattinson's process	74·71	74·70	74·74	per cent. MnO.

The values by the phosphate process are probably 0·1 per cent. high. Volhard's method is inclined to give too low values when the permanganate is standardised against iron or sodium oxalate. The permanganate should be standardised against manganese sulphate of known strength.[1] Gorgeu and Carnot[2] appear to think that the low values arise from the formation of a manganous manganite—$MnO.5MnO_2$—by the manganese in the solution, and this retards the further action of the permanganate on the manganous oxide under investigation. When zinc sulphate is present, zinc manganite—$ZnO.5MnO_2$—is formed, and this leaves only part of the manganese in solution to react with the permanganate. Bemmelen[3] considers that the precipitated manganic acid adsorbs part of the manganese salts in the solution, and so removes a little manganese from the "sphere of action" of the permanganate. He further assumes that when a zinc salt is present the zinc salt is adsorbed instead of the manganese salt.

The chief errors arise from the presence of organic matter; the addition of too much zinc oxide; and standardising the permanganate against iron instead of against manganese reduced from permanganate. Cobalt and chromium interfere with the process.

The method gives good results with compounds rich in manganese, although some object to the process, saying it gives erratic results. This criticism is too severe; when peculiarities of the method are understood, it is all right, and some analysts have said that they consider it to be "the simplest, quickest, and most accurate process for the volumetric determination of manganese."

Fischer's Modification of Volhard's Process.—This process, as recommended by Cahen and Little, is as follows:—The solution of the manganese salt in hydrochloric or sulphuric acid is neutralised with caustic soda until a slight precipitate persists on shaking. The precipitate is just redissolved by the addition of a drop or two of dilute sulphuric acid. Add 10 grms. of zinc sulphate and heat the mixture to boiling. Add 1 grm. of freshly ignited zinc oxide, and titrate with permanganate, with frequent heating nearly to boiling, until the permanganate is no longer decolorised. Cool the mixture under the tap for a minute or two, add 1–2 c.c. of glacial acetic acid, and thoroughly agitate the solution. The hot (not boiling) liquid is then titrated with permanganate, added a few drops at a time, with vigorous shaking after each addition, until the supernatant liquid retains its pink colour after being well shaken several times. The end point is easily observed, because the precipitate settles very quickly in the presence of acetic acid.

A difficulty arises during the titration unless the volume of the permanganate is known to within 3 or 4 c.c., owing to the slowness with which the finely divided oxide settles in the presence of zinc oxide. The time required for a titration is very long, and the end point is difficult to detect. If the acetic acid be added before any permanganate is added the result is too low, but the titration is rapidly effected, and the result serves as a guide for the titration proper.

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[1] See G. Auchy, *Journ. Amer. Chem. Soc.*, 18. 498, 1896; *Chem. News*, 74. 214, 248, 262, 1896.

[2] A. Gorgeu, *Bull. Soc. Chim.* (3), 9. 490, 1893; A. Carnot, *Compt. Rend.*, 116. 1375, 1893.

[3] J. M. van Bemmelen, *Journ. prakt. Chem.* (2), 23. 387, 1888.

The results leave little to be desired as far as accuracy is concerned. With two samples of pyrolusite, the following comparative results were obtained:

	No. 1.	No. 2.
Volhard-Fischer's process	48·75	50·35
Pattinson's process	48·72	50·50

§ 190. The Evaluation of Manganese Dioxide—Mohr's Process.

By the simultaneous action of sulphuric acid and an excess of ferrous sulphate or oxalic acid, the manganic dioxide is reduced to manganous sulphate, and the ferrous sulphate or oxalic acid is simultaneously oxidised. If known quantities of ferrous sulphate or oxalic acid be employed, the excess, not oxidised, can be determined by titration with standard permanganate.[1] The reaction with oxalic acid is represented:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

The following operations furnish sufficient data to calculate the amount of the manganese dioxide in the given sample.

The Determination.—Digest 0·4 grm. of finely divided, dry (110°)[2] sample in an Erlenmeyer's flask with 75 c.c. of a N-oxalic acid[3] or sodium oxalate solution, and 20 c.c. of sulphuric acid (1 : 4), until the black particles have passed into solution. Add about 200 c.c. of hot water (70°), and titrate the warm solution with approximately N-potassium permanganate until a permanent pink blush is suffused throughout the liquid. The titration is repeated as a blank experiment on 50 c.c. of the oxalic acid solution, and the volume of the permanganate corresponding with 75 c.c. calculated from the result.

Calculation.—From the equation representing the action of oxalic acid, or rather sodium oxalate, on potassium permanganate (page 194) and on manganese dioxide, it follows that $\frac{2}{5}$ of 158·03 grms. of $KMnO_4$ correspond with 86·93 grms. of MnO_2. Hence, 1 grm. of $KMnO_4$ represents 1·3752 grms. of MnO_2. Suppose that 1 c.c. of the permanganate solution has 0·0031606 grm. $KMnO_4$ per c.c., it follows that 1 c.c. of the permanganate solution will represent 0·0043464 grm. of MnO_2.

Suppose, in an experiment,

	$KMnO_4$ sol.
75 c.c. oxalic solution alone	75 c.c.
75 c.c. oxalic solution with sample	9 c.c.
0·4 grm. sample requires	66 c.c.

Hence, 0·4 grm. of sample has the equivalent of $66 \times 0·00435 = 0·287$ grm. MnO_2. Hence, the sample contains $\frac{1}{4} \times 0·287 \times 1000 = 71·7$ per cent. of MnO_2.

Errors.—The process indicated above represents the amount of oxygen—"available oxygen"—which is given off when the sample is decomposed by sulphuric acid, and since other manganese oxides—Mn_2O_3, Mn_3O_4, etc.—react in a similar way with the oxalic and sulphuric acids:

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[1] W. Hempel, *Mémoire sur l'emploi de l'acide oxalique dans les dosages à liqueurs titrées*, Lausanne, 1853; F. Mohr, *Zeit. anal. Chem.*, **8**. 314, 1869. R. Fresenius and H. Will (*Neue Verfahrungsweise zur Prüfung der Potasche, etc., sowie des Braunstein*, Heidelberg, 1843) determined the amount of manganese dioxide from the loss in weight due to the evolution of carbon dioxide; H. Kolbe (*Liebig's Ann.*, **119**. 130, 1861) absorbed the carbon dioxide in weighed potash bulbs; G. Bodländer (*Zeit. angew. Chem.*, **8**. 430, 1894) measured the volume of the gas evolved during the action of the acid.

[2] The sampling in bulk for moisture requires special attention (page 127). J. E. de Vry (*Liebig's Ann.*, **61**. 248, 1847); R. Fresenius, *Dingler's Journ.*, **135**. 277, 1855.

[3] Or 4·7 to 4·8 grms. of crystals of oxalic acid. The normal oxalic acid contains 63·024 grms. of the crystalline salt—$H_2C_2O_4 . 2H_2O$—per litre.

$$2Mn_2O_3 + 2H_2SO_4 + H_2C_2O_4 = 2MnSO_4 + 3H_2O + 2CO_2,$$
$$2Mn_3O_4 + 3H_2SO_4 + H_2C_2O_4 = 3MnSO_4 + 4H_2O + 2CO_2,$$

it follows that, if these oxides be present, the calculation might indicate more MnO_2 and less MnO than is really present. Some of the calculated MnO_2 might be present as Mn_2O_3, Mn_3O_4, etc. If the total manganese be determined as described on pages 376 or 377—Pattinson's or Volhard's process—the amount of MnO_2 multiplied by 0·816, and the product subtracted from the total MnO, will represent the approximate amount of manganese oxide—MnO—in the sample. If the pyrolusite contains reducing agents—ferrous oxide, carbonaceous matter, etc.,—low results will be obtained, because reactions are set up which reverse that produced by the peroxide.

Any ferrous iron which might be present will react with the permanganate and give low results by apparently diminishing the amount of oxalic acid broken down by the manganese dioxide. Carbonates do not interfere.

§ 191. The Colorimetric Determination of Manganese—Walter's Process.

The colorimetric determination of manganese is based upon the ease with which manganese solutions are oxidised to pink or violet permanganate. Brunner[1] fused the sample with alkali while exposed to an oxidising atmosphere, and deduced the amount of manganese from the intensity of the colour of the solution of the fused cake. The results by this method are not satisfactory. Lead peroxide,[2] sodium bismuthate,[3] and ammonium persulphate[4] are usually employed as oxidising agents. The manganese in the given solution is thus oxidised to pink permanganic acid. The intensity of the coloration depends upon the amount of manganese present. The tint of a test solution so prepared can be compared with the tint of a similar solution containing a known amount of manganese.[5] Something of the order 0·00001 grm. of manganese in 100 c.c. of solution can be determined by means of this process.

Preparation of the Standard Solution.—A stock solution of manganese sulphate containing 0·1 grm. of MnO per litre is prepared. Dissolve 0·2225 grm. of potassium permanganate in water; acidify with sulphuric acid; reduce with sulphurous acid; and make the solution up to a litre. Pipette sufficient of this solution—say 2 c.c.—into a 100-c.c. flask. Add 10 c.c. of silver nitrate solution (containing 2 grms. per litre), add 1 grm. ammonium persulphate, and warm on a water bath until a pink colour is developed. By the time the flask has cooled the colour will have acquired its maximum intensity. Make up to the 100-c.c. mark. Pipette from 2 to 10 c.c. into the test glass of the colorimeter.

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[1] A. Brunner, *Dingler's Journ.*, **210**. 278, 1873.

[2] T. M. Chatard, *Amer J. Science* (3), **1**. 416, 1871; *Chem. News*, **24**. 196, 1871; S. Peters, *ib.*, **33**. 35, 1876; *Dingler's Journ.*, **221**. 486, 1876; P. Picard, *Compt. Rend.*, **75**. 1821, 1872; A. Leclerc, *ib.*, **75**. 1209, 1872; *Chem. News*, **26**. 296, 1872; L. L. de Koninck, *Rev. Univ. Mines* (3), **5**. 308, 1889; T. E. Thorpe and F. J. Hambly, *Journ. Chem. Soc.*, **53**. 182, 1888; A. Ledebur, *Berg. Hütt. Ztg.*, **41**. 417, 1882; F. C. G. Müller, *Stahl Eisen*, **6**. 98, 1886; F. Osmond, *Bull. Soc. Chim.* (2), **43**. 56, 1885; Deshays, *Chem. News*, **38**. 70, 1878.

[3] L. Schneider, *Dingler's Journ.*, **269**. 224, 1893; L. Dufty, *Chem. News*, **84**. 248, 1901; J. Reddrop and H. Ramage, *Journ. Chem. Soc.*, **67**. 268, 1895; F. Ibbotson and H. Brearley, *Chem. News*, **82**. 269, 1900; **84**. 247, 302, 1901; **85**. 58, 1902; H. Ramage, *ib.*, **84**. 209, 269, 1901; **85**. 24, 95, 1902; A. A. Blair, *Journ. Amer. Chem. Soc*, **26**. 793, 1904; R. S. Weston, *ib.*, **29**. 1074, 1907; F. J. Metzger and R. F. M'Cracken, *ib.*, **32**. 1250, 1910; W. Blum, *ib.*, **34**. 1379, 1912; P. H. M. P. Brinton, *Journ. Ind. Eng. Chem.*, **3**. 237, 376, 1911; W. F. Hillebrand and W. Blum, *ib.*, **3**. 374, 1911; D. J. Demorest, *ib*, **4**. 19, 1912; J. R. Cain, *ib.*, **3**. 360, 1911; G. Bertrand, *Bull. Soc. Chim.* (4), **9**. 361, 1911; H. Rubricus, *Stahl Eisen*, **30**. 957, 1911; R. A. Gortner and C. O. Rost, *Journ. Ind. Eng. Chem.*, **4**. 522, 1912; F. J. Metzger and L. E. Marrs, *ib.*, **3**. 333, 1911; **5**. 125, 1913; H. F. U. Little, *Analyst*, **37**. 554, 1912.

[4] H. E. Walters, *Proc. Eng. Soc. West Pa.*, **17**. 257, 1901; *Journ. Amer. Chem. Soc.*, **25**. 392, 1903; **27**. 1550, 1905; *Chem. News*, **84**. 239, 1901; H. Marshall, *ib.*, **83**. 73, 1901; M. R. Schmidt, *Journ. Amer. Chem. Soc.*, **32**. 965, 1910; H. Rubricus, *Stahl Eisen*, **30**. 957, 1911; H. Kunze, *ib.*, **32**. 1914, 1912; P. Holland, *Chem. News*, **96**. 2, 1907; J. J. Boyle, *Journ. Ind. Eng. Chem.*, **4**. 202, 1912; M. Stanichitch, *Rev. Met.*, **8**. 891, 1911.

[5] The amount of permanganate in the test solution can also be verified volumetrically by titration with a standard solution of ferrous sulphate.

If insufficient silver nitrate has been added, a brown precipitate will be produced in the solution after the addition of the ammonium persulphate. In that case, add more sulphurous acid and more silver nitrate. Reoxidise with ammonium persulphate as before.

Preparation of the Test Solution.—The solution obtained by dissolving the cake from the pyrosulphate fusion; or the solution remaining after the colorimetric titanium determination; or the manganese sulphide can be dissolved in dilute sulphuric acid. The products from the pyrosulphate fusion generally contain chlorides, which must be removed before applying the test. Hence, it is usually quickest to assume that chlorides are present, and add a little silver nitrate solution to the boiling solution under investigation. Filter and wash the precipitate. Collect the filtrate and washings in a 200-c.c. flask; acidify the solution with sulphuric acid; add 10 c.c. of the silver nitrate solution as indicated above; and also add ammonium persulphate and warm as indicated for the preparation of the standard solution. When the solution is cold, make it up to the mark with water, and pour a quantity into the test glass of the colorimeter.

The Comparison.—The standard solution is diluted with water from a burette until an aliquot portion has the same tint as the test solution. The amount of water required for the purpose is measured. See iron, page 200, for further details.

Calculations.—Suppose that 2 c.c. of the standard solution of manganese sulphate was made up to 100 c.c., and that 5 c.c. of this solution required the addition of 83 c.c. of water to bring it to the same tint as the test solution.

1 c.c. standard has 0·0001 grm. MnO; ∴ 2 c.c. has 0·0002 grm.; this diluted to 100 c.c. has 0·000002 grm. MnO per c.c.; 5 c.c. of this required 83 c.c. water, so that $5 + 83 = 88$ c.c. of the solution has 0·00001 grm. MnO, and 200 c.c. has

$$\frac{200 \times 0{\cdot}00001}{88} = 0{\cdot}00002 \text{ grm. MnO.}$$

But the clay was made up to 250 c.c., and 100 c.c. was taken; hence,

$$\frac{250 \times 0{\cdot}0002}{150} = 0{\cdot}00004 \text{ grm.; or } 0{\cdot}004 \text{ per cent. MnO.}$$

With practice, and normal colour vision, differences of tint corresponding with 0·00001 grm. of MnO can be detected. If the quantity of manganese in the portion of the sample under investigation is less than 0·001 grm., it is well to work with a larger quantity of the sample. The results with quantities of manganese over about 2 per cent. are not so good as by gravimetric or volumetric processes. The presence of a little iron seems to favour the oxidation of the manganous oxide, MnO, to the permanganate. Jervis[1] shows that the colour is more intense with increasing amounts of manganese up to a certain maximum, and after that a decrease in the intensity of the colour occurs with increasing amounts of manganese. Thus:

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[1] H. Jervis, *Chem. News*, 81. 171, 1900.

$MnSO_4$ added	2	10	20	30	40	50	c.c.
$KMnO_4$ found with iron . .	3·45	14·8	24·7	21·0	13·75	8·0	c.c.
$KMnO_4$ found, no iron . .	3·35	16·45	25·85	22·9	18·0	12·15	c.c.

Aluminum and molybdenum do not interfere; copper and nickel exercise no further influence than that due to the colour of their salts.

The Effect of Chromium Salts.—If chromium be present, the yellow colour of the chromate produced by the oxidising action of the persulphate spoils the tint of the permanganate, and the chromium must be removed before the comparison can be made. Dittrich[1] does this by boiling the discoloured solution with ammonia for a short time,—iron and manganese hydroxides are precipitated, and the chromium remains in solution as chromate. Filter and wash. Remove the silver from the filtrate by the addition of common salt; again filter and wash. Evaporate the filtrate down to between 50 and 100 c.c. and estimate the chromium as indicated on page 473. The manganese precipitate on the filter paper is dissolved in dilute sulphuric acid mixed with some sulphurous acid or hydrogen peroxide. The manganese is then determined colorimetrically as indicated above.

§ 192. The Analysis of Wads, and Manganese Earths.

Manganese peroxide is mainly used in the manufacture of chemicals, in glass-making, and for the manufacture of dry batteries. There are many manganese ores which serve excellently for the manufacture of pottery colours and yet contain little or no peroxide. Mohr's process is not then applicable. These ores are usually sold on a basis of 50 units of manganese[2]—one unit means 1 per cent.—at so much per unit, with a bonus or penalty per unit respectively above or below 50. A maximum of, say, 8 per cent. silica and 0·2 per cent. phosphorus may be allowed, with a deduction of, say, ½d. per unit of silica above the maximum, and an agreed deduction for each 0·02 per cent. of phosphorus above the agreed maximum.[3] The Caucasian, Indian, and Brazilian ores are fairly constant in composition, and run from about 50 to 55 per cent. manganese, 0·03 per cent. phosphorus, and 10 per cent. silica; the Turkish and Japanese ores run from 43 to 56 per cent. manganese, 0·5 per cent. phosphorus, and 7 to 10 per cent. silica. Japanese "brown stone" may run as much as 87 per cent. MnO_2, and such an ore sells for twice as much as 70 per cent. ore.[4]

Dissolution of the Solid.—Digest 1 grm. of the sample in a 250-c.c. Erlenmeyer's flask with concentrated hydrochloric acid. The attack generally begins in the cold. When the first action is over, gradually warm the flask up to the boiling point. It may be necessary to add a little more acid to complete the action. Add water and filter. The insoluble matter may be light-coloured silica, or some dark-coloured mineral not decomposed by the acid. The filter paper and contents should be ignited in a weighed platinum crucible and weighed. This may be reported as "sand and insoluble matter," or fused with alkaline carbonate in an oxidising atmosphere. If the mass on cooling is white or pale greenish blue in tinge, it may be rejected. If the fused mass be green, dissolve in hydrochloric acid, evaporate to dryness, and take up with water and hydrochloric acid as indicated on page 164. Add the filtrate from the silica to the main solution. The silica may be determined in the usual manner.

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[1] M. Dittrich, *Zeit. anorg. Chem.*, **80**. 171, 1913

[2] Pure manganous oxide, MnO, runs 77·5 per cent. manganese (Mn); the dioxide, MnO_2, 63·2 per cent.; the sesquioxide, Mn_2O_3, 69·6 per cent.; and the manganomanganic oxide, Mn_3O_4, 72·0 per cent.

[3] *E.g.*, one consumer recently purchased its ore on the following basis (1911):—Ores with 50 per cent. Mn to be purchased (delivered) at 13d. per unit per ton; 46–50 per cent. Mn, 12½d.; 43–46 per cent. Mn, 12d.; 40–43 per cent., 11½d. For each per cent of silica above the maximum 8 per cent., deduct 7½d. per ton, and for each 0·02 per cent. phosphorus above 0·2 per cent., deduct 1d. per unit of manganese per ton. Sample for analysis to be dried at 100°; the percentage of moisture in the sample to be deducted from the weight.

[4] G. T. Holloway, *Trans. Inst. Min. Met.*, **21**. 569, 1912.

Removal of Alumina and Iron Oxide.—Precipitate the joint alumina, ferric oxide, and phosphoric oxide by the sodium acetate process (page 362) from a solution acidified with acetic acid. If much manganese be present, two, three, or four precipitations may be necessary. If the combined filtrates exceed 300 c.c., evaporate to about 200 c.c. If a white precipitate separates during the evaporation, it may be neglected; but if a reddish precipitate separates, it must be filtered off, dissolved in hydrochloric acid, the iron precipitated as basic acetate, and the filtrate added to the main filtrate. The alumina, iron, and phosphoric oxide may be treated by the methods of page 177.

Precipitation of Manganese.—Add approximately 5 grms. of sodium acetate—15 c.c. of solution—and 2 or 3 c.c. of liquid bromine. If a saturated aqueous solution of bromine be used, the solution may become rather bulky. The solution should have a yellow tint, showing that an excess of bromine is present. Filter. Add more bromine to the filtrate and boil again. This ensures the complete precipitation of the manganese. If any precipitate be formed, filter. The precipitated manganese is dissolved in a hot dilute solution of nitric acid to which is added either sulphurous acid or a little sodium bisulphite. The reducing agent facilitates the solution of the precipitate. The manganese may now be determined in the solution by volumetric, colorimetric, or gravimetric processes. If needed, the lime and magnesia can be determined in the combined filtrates.

Determination of Carbon.—Dissolve 10 to 20 grms. of the ore in concentrated hydrochloric acid as indicated above. Dilute with water. Filter the residue through a Gooch's crucible charged with ignited asbestos, wash, dry at 110°, and weigh the crucible and contents. Burn off the carbon, and re-weigh. The loss in weight represents the organic matter. To eliminate the obvious errors, the asbestos may be ignited and the resulting carbon dioxide determined as indicated on page 563. The wet combustion process may also be employed as indicated on page 546.

CHAPTER XXIX.

THE DETERMINATION OF COBALT AND NICKEL.

§ 193. The Detection of Cobalt and Nickel.

The usual scheme for the qualitative analysis of mixtures leaves finally a precipitate containing the mixed sulphides of cobalt and nickel. There are several distinguishing tests. To get the sulphides into solution, boil the filter paper and contents in a small flask with 10 c.c. of hydrochloric acid (1 : 4) and 1 c.c. of nitric acid (1 : 3). Filter off the precipitated sulphur and the filter paper. Collect the filtrate in a basin, and evaporate to dryness to expel the excess of acid. Dissolve the residue in two or three drops of hydrochloric acid and 10 c.c. of water.

Tests for Cobalt. (1) *Ilinsky and Knorre's Test.*[1]—Add a slight excess of a saturated solution of nitroso-β-naphthol (page 394) in acetic acid. Agitate the solution. A brick-red precipitate represents cobalt. Confirm as usual.

(2) *Skey's Test.*[2]—Add a saturated solution of potassium thiocyanate and shake up the mixture with a mixture of amyl alcohol and ether. The ethereal layer will be blue if 1 c.c. of a 1 : 50,000 aqueous solution be used.

(3) *Danziger's Test.*[3]—To about 5 c.c. of the colourless solution, acidified with hydrochloric acid, add a little solid ammonium thio-acetate—$CH_3 . COSNH_4$—a few drops of stannous chloride,[4] and an equal volume of amyl alcohol, or a mixture of acetone and ether, or alcohol and ether. Shake. Let settle. If cobalt be present, the upper layer will be coloured blue. This test will indicate 1 part of cobalt in 500,000 parts of water, and is more delicate than Skey's test.

Tests for Nickel. (1) *Tschugajeff's Test.*[5]—If an excess of dimethylglyoxime be added to a strongly ammoniacal solution containing a mixture of cobalt and nickel, and the solution be boiled a short time, a rose coloration or a scarlet-red precipitate will be obtained, according to the amount of nickel present (page 394). This reagent is reported to detect nickel in 1 c.c. of a 1 : 200,000 solution, or in 4 c.c. of a 1 : 500,000 solution.

(2) *Parr's Test.*[6]—Freshly precipitated nickel hydroxide liberates iodine from potassium iodide, but the corresponding cobalt compound does not. Hence,

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[1] M. Ilinsky and G. von Knorre, *Ber.*, **18**. 699, 1885.

[2] W. Skey, *Chem. News*, **16**. 201, 1867. This is generally, but incorrectly, called "Vogel's test." H. W. Vogel, *Ber.*, **8**. 1533, 1875 ; **12**. 2314, 1879 ; F. P. Treadwell, *Zeit. anorg. Chem.*, **26**. 108, 1901. See page 397.

[3] J. L. Danziger, *Journ. Amer. Chem. Soc.*, **24**. 578, 1902.

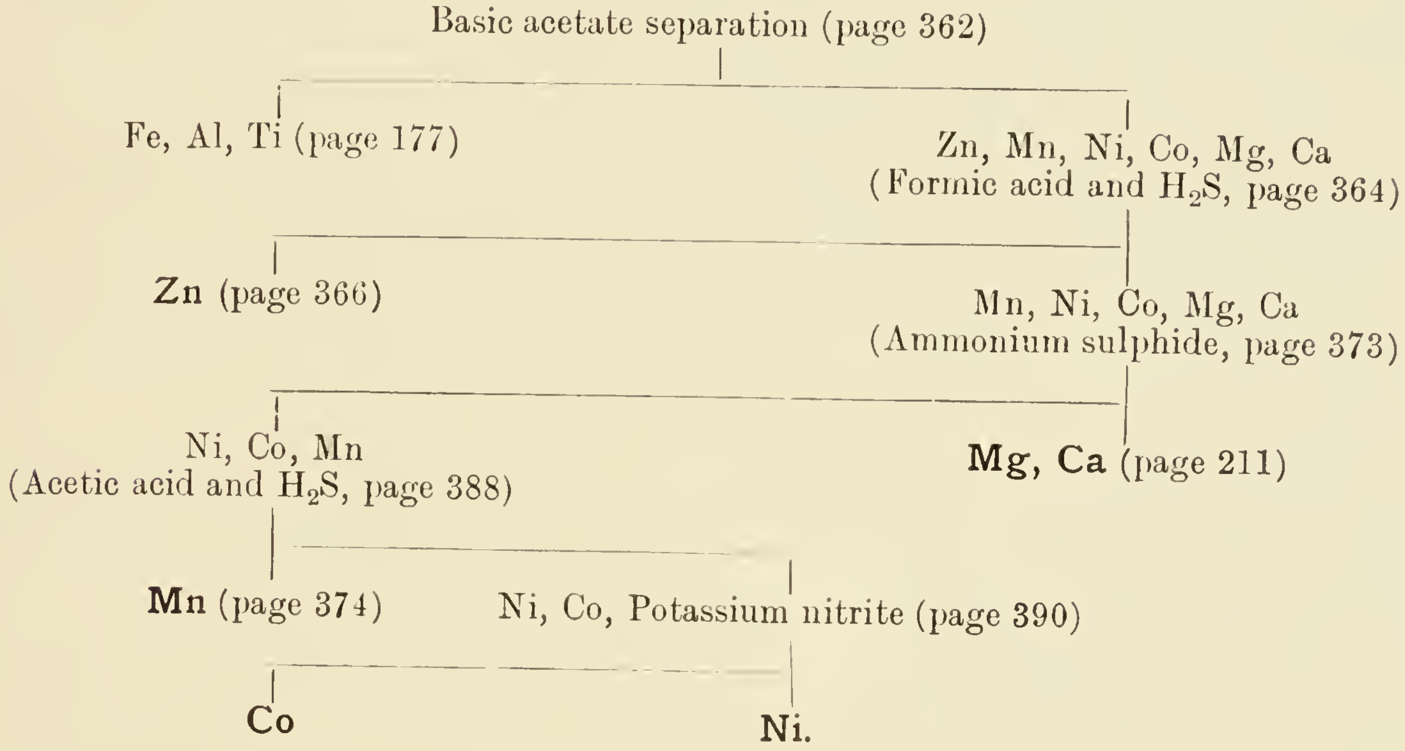
[4] To reduce the ferric salts which give a red colour. The solid ammonium thio-acetate ensures a concentrated solution.

[5] L. Tschugajeff, *Ber.*, **38**. 2520, 1905. For the sensitiveness of different tests for cobalt and nickel, see A. del Campo y Cerdan and J. Ferrer, *Anales Soc. Espan. Fis. Quim.*, **9**. 201, 272, 1911 ; S. R. Benedict, *Journ. Amer. Chem. Soc.*, **27**. 1360, 1905.

[6] S. W. Parr, *Journ. Amer. Chem. Soc.*, **19**. 341, 1897 ; S. R. Benedict, *ib.*, **26**. 695, 1904.

add bromine water to the solution containing either cobalt or nickel; warm the solution; add an excess of sodium hydroxide, and boil. Filter. Wash the precipitated hydroxide on a filter paper. Pour a hot solution of potassium iodide through the paper. Free iodine in the filtrate is evidence of nickel. The iodine is best detected by shaking up the filtrate with a little benzene.

The separation of cobalt and nickel is not usually of any particular importance in silicate analyses, but the methods here indicated represent the type of what is wanted in colour and glaze analyses. The analysis of cobalt oxides is more frequently wanted than nickel. The scheme for the separation of iron, aluminium, titanium, zinc, manganese, nickel, cobalt, magnesia, and lime may be summarised (solids to left, solutions to right):—


Basic acetate separation (page 362)
Fe, Al, Ti (page 177)
Zn, Mn, Ni, Co, Mg, Ca
(Formic acid and H_2S, page 364)
Zn (page 366)
Mn, Ni, Co, Mg, Ca
(Ammonium sulphide, page 373)
Ni, Co, Mn
(Acetic acid and H_2S, page 388)
Mg, Ca (page 211)
Mn (page 374)
Ni, Co, Potassium nitrite (page 390)
Co
Ni.

§ 194. The Properties of Cobalt and Nickel Sulphides.

Simultaneous Precipitation of Traces of Cobalt and Nickel with the Alumina and Iron.—The addition of ammonium chloride prevents, to a great extent, the precipitation of cobalt and nickel by ammonia; but if insufficient ammonium chloride be present, some nickel and cobalt may be carried down with the aluminium and iron hydroxides. Baumhauer[1] determined the amount of cobalt and nickel which were precipitated along with the iron when known mixtures of iron, cobalt, and nickel were treated with the regular precipitating agents. He found:

	Per cent. nickel.	Per cent. cobalt.
Ammonia (page 177)	27	48
Sodium acetate process (page 362) . .	18	9
Barium carbonate in the cold (page 470) .	8	15

But even when plenty of ammonium chloride is present, appreciable amounts may be precipitated with the iron and alumina as well as with the zinc. If these leakages are not guarded against by double precipitations,[2] the loss of cobalt and nickel, when precipitated at the end of a complex series of separations, may be quite serious.

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[1] E. H. von Baumhauer, *Zeit. anal. Chem.*, **10**. 217, 1871.

[2] T. Moore, *Chem. News*, **65**. 75, 1892; A. Thomas, *ib.*, **35**. 187, 1877; T. H. Laby, *ib.*, **89**. 280, 1904; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **41**. 616, 1894. For clean separations with a large excess of ammonium chloride, see J. T. Dougherty, *Chem. News*, **95**. 261, 268, 1907; V. Hassreidter, *Zeit. angew. Chem.*, **22**. 1492, 1909. According to F. Ibbotson and H. Brearley (*Chem. News*, **81**. 193, 1900), the nickel is absorbed by the precipitated ferric hydroxide in the same way that filter paper absorbs salts from a solution; the nickel is absorbed from ammoniacal solutions only because nickel is removed from the precipitate by making the solu-

In the present case, the iron, aluminium, and titanium are separated by the ammonia or the basic acetate process; the zinc as zinc sulphide; and finally the cobalt and nickel are precipitated as sulphides from a solution acidified with acetic acid. Manganese is not precipitated under these conditions. There is need for a few special remarks on the sulphides of nickel and cobalt.

Action of Ammonium Polysulphide on Nickel and Cobalt Salts.—These elements are not precipitated by hydrogen sulphide from solutions acidified with the mineral acids, but the sulphides are precipitated in the presence of acetic acid, particularly if ammonium or sodium acetate be present and the solution is warm. Ammonium sulphide precipitates the black or dark brown-coloured sulphides from neutral or ammoniacal solutions of nickel and cobalt. The precipitate is but sparingly soluble in acetic acid, and in very dilute hydrochloric acid. If yellow ammonium sulphide be employed, that is, ammonium polysulphide, more or less nickel sulphide passes into solution and the filtrate will be coloured brown. It is generally supposed that either a soluble complex ammonium thionickelate, $(NH_4)_2NiS_{2+n}$, or a colloidal nickel persulphide is formed. The greater the excess of ammonium sulphide and the longer the solution is exposed to the air, the greater the tendency of the nickel to pass into solution in this manner.[1]

Action of Ammonium Monosulphide on Nickel Salts.—In the presence of ammonium hydroxide, colourless ammonium sulphide forms a violet-coloured solution with nickel salts. This soon becomes red, dark brown, and finally a black precipitate separates. On filtration, the filtrate appears colourless; but if the colourless solution be heated, a black precipitate of nickelous sulphide separates. Free ammonia is not necessary for this action. Colourless ammonium sulphide, free from the polysulphide, precipitates nickel completely as sulphide, and the filtrate, in the absence of air, will be free from nickel and colourless. Ammonium monosulphide rapidly oxidises to polysulphide when exposed to the air, and it is almost impossible to prevent some nickel passing into the filtrate, particularly when working with large quantities of this metal. It is useless to try and get the brown solution clear by filtration. The best method of dealing with the coloured filtrate is to coagulate the nickel sulphide by 5 or 10 minutes' boiling; re-filtration is then generally successful. These troubles are alleviated by passing hydrogen sulphide into the warm ammoniacal solution.

If the solution of nickel be free from foreign salts—ammonium chloride, etc.—colourless ammonium sulphide forms a brown colloidal solution of the sulphide which passes through the filter paper. The sulphide is then precipitated by adding, say, ammonium chloride.

Action of Acids upon Nickel and Cobalt Sulphides.—These sulphides, once

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tion so slightly acid that the ferric hydroxide is scarcely dissolved; and less nickel is absorbed by increasing the amount of ammonium salt—chloride, nitrate, or sulphate—in the solution, and decreasing the amount of ammonia. If, therefore, the precipitation of ferric hydroxide be made in presence of ammonium chloride, and so little ammonia that the filtrate is perceptibly acid, the separation of iron and nickel is a "good one." Schwarzberg's method of separation (P. Schwarzberg, *Liebig's Ann.*, **97**. 216, 1856; J. F. W. Herschel, *Ann. Chim. Phys.* (3), **49**. 306, 1837) depends on the nice adjustment of the "neutralisation" so that the fluid loses its transparency without showing the least trace of a distinct precipitate, and fails to recover its clearness after standing some time; the solution is boiled, and the iron hydroxide is said to be precipitated comparatively free from nickel (R. Fresenius, *Quantitative Chemical Analysis*, London, **1**. 437, 1876).

[1] A. Lecrenier, *Chem. Ztg.*, **13**. 436, 449, 1889; R. Fresenius, *Journ. prakt. Chem.* (1), **82**. 257, 1861; A. Villiers, *Compt. Rend.*, **119**. 1208, 1263, 1894; U. Anthony and G. Magri, *Gazz. Chim. Ital.*, **31**. ii., 265, 1901.

formed, are generally said to be insoluble in acetic and hydrochloric acids. The alleged "insolubility" is a misnomer, because relatively large amounts of the two sulphides do dissolve in dilute hydrochloric acid—1 volume acid, sp. gr. 1·12, with 5 volumes of water.[1] The reverse action, the precipitation of the sulphides in acid solution by hydrogen sulphide, is also exceedingly slow. If over a trace of acetic or hydrochloric acid be present, neither sulphide will be precipitated in the cold; but if the solution be hot, both nickel and cobalt sulphides will be precipitated in the presence of ammonium or sodium acetate. Cobalt and nickel sulphides become "insoluble" in these acids on standing for some time, or on heating. They then require digesting with aqua regia for their solution.[2]

§ 195. The Separation of Manganese from Cobalt and Nickel.

Precipitation of Nickel, Cobalt, and Manganese Sulphides.[3]—The filtrate from the zinc sulphide is neutralised with ammonia, and an excess of ammonia (free from carbonate) is added to the solution. Hydrogen sulphide is passed through the warm (70°–80°) solution, whereby the mixed sulphides of manganese, cobalt, and nickel[4] are precipitated. The alkalies and alkaline earths remain in solution. Filter[5] at once,[6] and wash with water containing a little ammonium sulphide and chloride in solution.

The filtrate may come through brown. In any case—clear or brown—evaporate the filtrate to about 50 c.c.; add freshly prepared ammonium sulphide; acidify with acetic acid; and boil for some time. This will curdle the sulphides not retained on the filter paper, and allow them to be readily removed by filtration. The danger of losing nickel and cobalt sulphides is here so serious that, if any metal escaped with the first filtrate, it is advisable to test the filtrate again to make sure that all the cobalt and nickel have been precipitated.

Precipitation of Nickel and Cobalt Sulphides.—The washed precipitate is dissolved in aqua regia, and boiled to expel the excess of acid. Add an excess of sodium carbonate to the solution, and then acetic acid[7] until the solution is faintly acid. Add 3 to 5 grms. of sodium or ammonium acetate;[8] dilute the solution to, say, 200 c.c.; pass hydrogen sulphide through the warm solution (70°–80°). The sulphides of cobalt and nickel[9] are precipitated, the manganese remains in solution. Filter at once through a close-packed filter paper, and wash with hydrochloric acid (sp. gr. 1·025) saturated with hydrogen sulphide in order to remove any manganese sulphide precipitated with the cobalt and nickel sulphides.

The risk of losing cobalt, and particularly nickel, is here very great. Hence, make sure that the precipitation is complete by evaporating the clear filtrate to 50 c.c.; add an excess of ammonium sulphide; acidify with an excess of acetic acid, and warm the solution. If nickel or cobalt be present, a precipitate will be formed. Filter. Test the filtrate as before. When all the cobalt and nickel has been precipitated, wash as before.[1]

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[1] H. Baubigny, *Compt. Rend.*, **94**. 963, 1183, 1251, 1417, 1473, 1715, 1882; **95**. 35, 1882; **105**. 751, 806, 1887; **106**. 132, 1888; *Chem. News*, **57**. 55, 1888.

[2] W. Herz, *Zeit. anorg. Chem.*, **27**. 390, 1901; **28**. 342, 1901.

[3] R. Fresenius, *Anleitung zur quantitativen Analyse*, Braunschweig, I. 579, 1875; London, I. 429, 1876.

[4] Also copper, if present.

[5] A close-packed filter paper must be used, say, C. Schleicher and Schüll's No. 589, or M. Dreverhoff's No. 331.

[6] All sulphides precipitated from boiling solutions should be filtered and washed at once, so as to prevent oxidation. S. P. Sharples, *Amer. J. Science* (2), **50**. 248, 1870; *Chem. News*, **22**. 259, 1870.

[7] W. Funk (*Zeit. anal. Chem.*, **45**. 562, 1906) uses formic acid.

[8] Say 5 grms. of ammonium acetate per gram of cobalt or nickel.

[9] Also copper, zinc, and uranium, if present. W. Gibbs, *Amer. J. Science* (2), **39**. 62, 1865; *Chem. News*, II. 147, 1865.

Dry the filter paper and contents. Incinerate to burn off the paper. Dissolve the precipitate in hydrochloric acid mixed with a little nitric acid, and determine the nickel and cobalt separately as indicated below.

§ 196. The Separation of Cobalt and Nickel—Fischer's Nitrite Process.

Fischer's process[2] depends on the formation of an "insoluble" potassium cobaltinitrite—Fischer's salt—under conditions where the corresponding nickel salt is soluble. If necessary, evaporate the solution containing the mixed cobalt and nickel salts to dryness. Take up the residue with one or two drops of concentrated hydrochloric acid, and as little water as possible. It is said that the presence of two parts of cobalt per million can be detected in this way.

Precipitation of Potassium Cobaltinitrite.—Add caustic potash[3] to the solution under investigation until the precipitate is no longer formed on adding another drop of alkali. The solution will then have an alkaline reaction. Acidify the solution with an excess of acetic acid.[4] Suppose that the total volume is between 5 and 10 c.c. Add half this volume of a 50 per cent. solution of potassium nitrite,[5] and stir the solution vigorously. Let the solution stand for 24 hours in a warm place. Test if the precipitation is complete by pipetting off a little clear solution and adding a little more potassium nitrite. If precipitation be not complete, transfer the small portion back to the main solution, and repeat the treatment with the potassium nitrite solution, etc.

Filter the solution containing the yellow crystalline precipitate.[6] Use the clear filtrate for washing the precipitate on to the filter paper. Wash the precipitate with a barely acid 5 per cent. solution of potassium nitrite[7] until

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[1] The manganese in the filtrate from the nickel and cobalt sulphides is determined as indicated on page 374.

[2] A. Duflos and N. W. Fischer, *Pogg. Ann.*, **72**. 475, 1847 ; **74**. 115, 1849 ; H. Rose, *ib.*, **110**. 411, 1860 ; A. Stromeyer, *Liebig's Ann.*, **96**. 218, 1855 ; W. Gibbs and F. A. Genth, *ib.*, **104**. 309, 1857 ; *Chem. News*, **28**. 51, 1873 ; H. Baubigny, *Ann. Chim. Phys.* (6), **17**. 103, 1889 ; F. Gauhe, *Zeit. anal. Chem.*, **4**. 56, 1865 ; **5**. 74, 1866 ; A. Brauner, *ib.*, **16**. 195, 1877 ; O. Brunck, *Zeit. angew. Chem.*, **20**. 834, 1847, 1907 ; H. Herrenschmidt and E. Capilli, *Le Cobalt et le Nickel*, Rouen, 1888 ; *Chem. News*, **69**. 112, 128, 142, 1894 ; *Zeit. anal. Chem.*, **32**. 607, 1893 ; W. Funk, *ib.*, **46**. 1, 1907.

[3] Some of the very best grades of caustic alkali contain nickel derived from the dishes in which the alkalies were made. Iron, alumina, and silica also appear in all but the very best grades of caustic alkali.

[4] L. L. de Koninck (*Bull. Soc. Chim. Belg.*, **23**. 11, 200, 1909) considers that the precipitation is more complete if the solution contains a little free nitric acid and more potassium nitrite is added than suffices to neutralise the nitric acid.

[5] Potassium Nitrite Solution.—1 grm. of the salt per 2 c.c. of water, and just neutralise the solution with acetic acid. The solution is prepared for use as required. If the solution has any flecks of insoluble alumina or silica, filter. Always test each batch of potassium nitrite for silica, alumina, and lead before it is used.

[6] If alkaline earths, copper, or lead be present, some nickel may be precipitated with the cobalt owing to the formation of triple nitrites of lead, potassium, nickel, and the third element. It is also important to use freshly prepared ammonium sulphide, or ammonia free from carbonates, in separating the alkaline earths from the ammonium sulphide group. H. Baubigny, *Compt. Rend.*, **107**. 1148, 1888. Zinc and cadmium do not give precipitates when treated by the nitrite process.

[7] Some recommend washing with a 10 per cent. solution of potassium acetate containing a little potassium nitrite, because the potassium acetate can be removed by washing with alcohol, in which it is fairly soluble, while potassium nitrite is but sparingly soluble in this solvent. B. Brauner, *Zeit. anal. Chem.*, **16**. 195, 1877. There is no need for the alcohol washing here, and potassium nitrite alone gives better results.

1 c.c. of the wash-water boiled with hydrochloric acid and treated with caustic potash and bromine gives no black precipitate of nickel hydroxide, or until a portion of the filtrate neutralised with ammonia is not coloured brown with ammonium sulphide.

Precipitation of Cobalt Hydroxide.—Transfer the precipitated potassium cobaltinitrite[1] to a porcelain dish, cover with a clock-glass, and add hydrochloric acid until no more nitric oxide is evolved, showing that the nitrite is decomposed. Treat the solution with an excess of caustic potash and bromine;[2] take care that the solution is kept alkaline with potash. The cobalt is precipitated as black cobalt hydroxide. Filter through a close-packed filter paper and wash by decantation with hot water. Dry and ignite the filter paper and precipitate in a Rose's crucible. Cool and weigh. Ignite the contents of the crucible in a stream of hydrogen, and weigh as metallic cobalt.[3]

Purification from Silica.—Owing to the large amount of alkali used in these determinations, the precipitates are particularly liable to contamination with silica and alumina from the glass, etc. To remove the silica, treat the oxide with hydrochloric acid in a porcelain crucible; evaporate the mass to dryness; mix with concentrated hydrochloric and nitric acids; add hot water; filter; wash with hot water; ignite the paper and contents; and weigh as silica—SiO_2. Dede[4] claims that if potassium or sodium persulphate is used in place of bromine, so slight an excess of alkali hydroxide is needed that the precipitated cobalt (or nickel) oxides can be easily washed.

Ignition in a Rose's Crucible.—Rose's crucible[5] has an opening in the lid for the introduction of an earthenware pipe *A* for leading gas into the red-hot crucible.[6] The arrangement for this particular experiment is indicated in fig. 138. The hydrogen[7] is generated in a Kipp's apparatus, *B*. The hydrogen should be freed from arsenic, antimony, phosphorus, and carbon compounds by washing in a solution, *C*, of potassium permanganate in concentrated sulphuric acid; from sulphur compounds by washing in a concentrated solution of caustic soda, *D*; and dried by passing through a tower of calcium chloride, *E*.[8]

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[1] O. L. Erdmann, *Journ. prakt. Chem.* (1), 97. 397, 1866; M. St Evre, *ib.* (1), 54. 84, 1851; *Compt. Rend.*, 33. 166, 1851; A. Remelé, *Zeit. anal. Chem.*, 3. 313, 1864; W. Braun, *ib.*, 6. 72, 1867; 7. 313, 1868; A. Rosenheim and I. Koppel, *Zeit. anorg. Chem.*, 17. 35, 1898; R. Wegscheider, *ib.*, 49. 441, 1906; T. Rosenbladt, *Ber.*, 19. 2535, 1886; S. P. Sadtler, *Amer. J. Science* (2), 49. 189, 1870; *Chem. News*, 22. 8, 15, 26, 1870; W. Blomstrand, *Chemie der Jetztzeit*, Heidelberg, 414, 1869.

[2] L. Dede (*Chem. Ztg.*, 35. 1077, 1911) recommends sodium or potassium persulphate in place of bromine, since only enough alkali is then needed to ensure alkalinity after the addition of the persulphate. The precipitation occurs in cold after standing one or two hours with frequent shaking.

[3] T. Bayley, *Chem. News*, 34. 81, 1876; A. Carnot, *ib.*, 59. 183, 1889; *Compt. Rend.*, 108. 741, 1889; B. Brauner, *Zeit. anal. Chem.*, 16. 195, 1877.

[4] L. Dede, *Chem. Ztg.*, 35. 1077, 1911.

[5] H. Rose, *Pogg. Ann.*, 110. 128, 1860. In the absence of a Rose's crucible, an ordinary crucible and a common clay pipe of such a size that the mouth of the inverted bowl will just pass into the crucible may be used. E. Murmann (*Monats. Chem.*, 19. 403, 1898) has a Gooch's crucible with a tube extension below the perforated base whereby the sulphide can be filtered as in Gooch's crucible, and subsequently heated in a current of any desired gas. The tubes are easily broken, and they are therefore expensive.

[6] W. Gibbs (*Chem. News*, 28. 30, 1873; R. H. Lee, *ib.*, 24. 234, 1871; *Amer. J. Science* (3), 2. 44, 1871) recommends a circular disc of porous earthenware above the substance to be heated, and below the gas inlet pipe. The gases pass through the disc to the substance to be reduced by diffusion. Mechanical loss is thus prevented. The "soft" porous capsule can be easily filed to fit the crucible perfectly.

[7] Not coal gas, because of the formation of cobalt carbides.

[8] E. Schobig, *Journ. prakt. Chem.* (2), 14. 289, 1877; E. Varenne and E. Hebre, *Bull. Soc. Chim.* (3), 28. 523, 1902.

Explosions may be prevented by placing a glass tube containing cotton-wool between discs of wire gauze immediately after the drying tower.[1] See page 150.

The Rose's crucible is placed in position, and when the air has been expelled by the hydrogen generated in the Kipp's apparatus, light the burner and gradually raise the temperature of the crucible and contents to bright redness.[2] The current of gas [3] should be so regulated that from about two to four bubbles per second pass through the wash-bottle during the earlier stages of the reduction, when comparatively large volumes of steam are being evolved. The velocity of the stream may then be increased to about eight bubbles per second. In about 10 or 15 minutes the oxide will no doubt be all reduced to metal; remove the flame; and let the crucible cool in the current of gas. Place the crucible in a desiccator, and, when cold, weigh as metallic cobalt. For example:

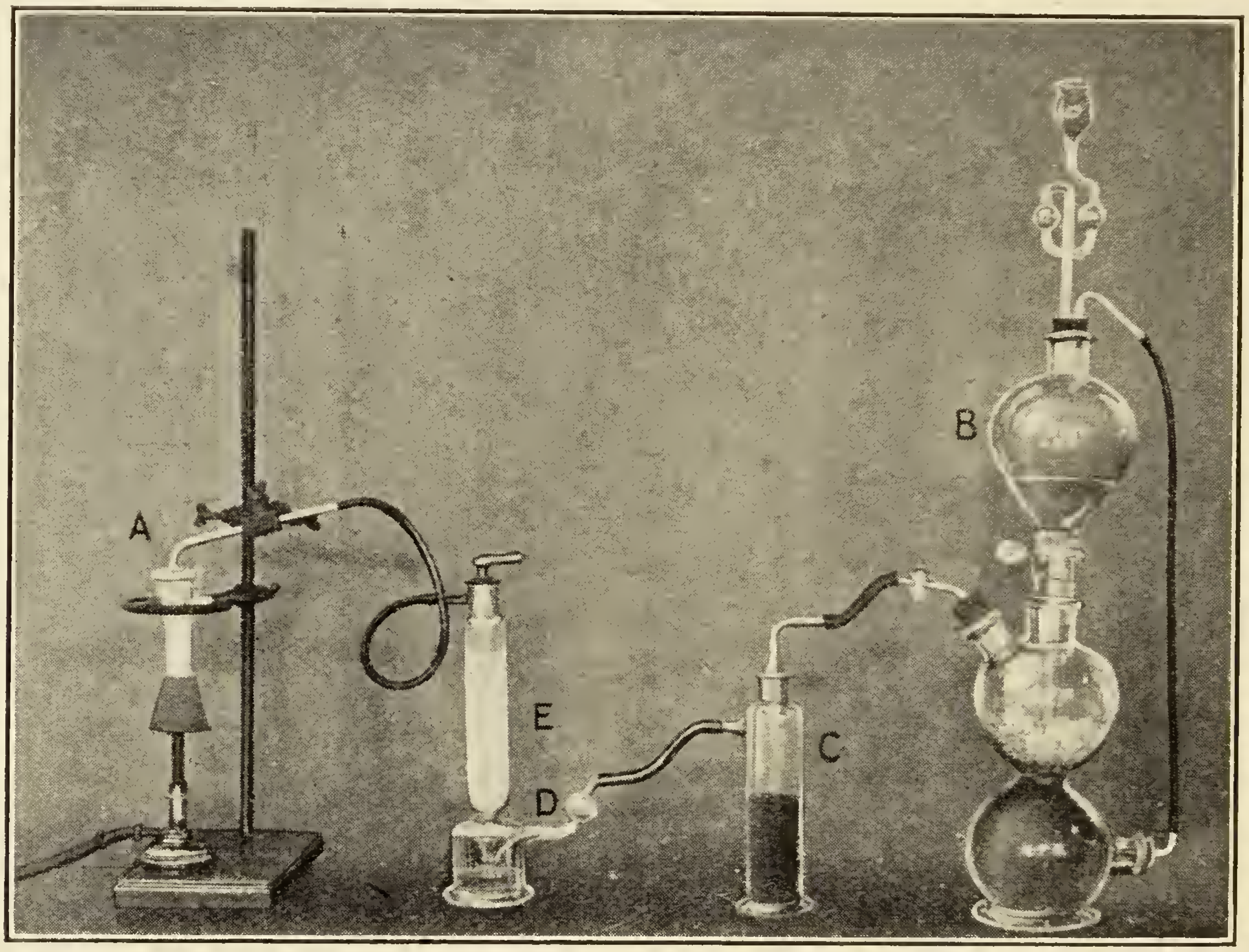

Fig. 138.—Reduction of cobalt oxide.

Rose's crucible plus metal	15·3572 grms.
Rose's crucible alone	14·8731 grms.
Metallic cobalt	0·4841 grm.

The reduction is necessary because oxides of varying degrees of oxidation are formed by the ignition in air. Some prefer to convert the oxides into sulphates before weighing, and thus avoid the reduction.[4]

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[1] R. Fresenius, *Zeit. anal. Chem.*, **12**. 73, 1873; C. G. Hopkins, *Journ. Amer. Chem. Soc.*, **21**. 645, 1899; *Chem. News*, **81**. 134, 1900.

[2] The reduction of cobalt oxide commences about 132°—W. Müller, *Pogg. Ann.*, **136**. 51, 1869.

[3] J. Habermann (*Zeit. anal. Chem.*, **28**. 88, 1889) recommends an alloy of tin with 83–84 per cent. of zinc in preference to zinc alone. The form of Habermann's alloy remains the same after the zinc has dissolved, and in consequence none falls into the lower bulb of Kipp's generator.

[4] E. J. Maumené, *Compt. Rend.*, **79**. 179, 1874; F. Gauhe, *Zeit. anal. Chem.*, **4**. 53, 1865; W. J. Russell, *Journ. Chem. Soc.*, **16**. 51, 1863.

Determination of Nickel.—The nickel is determined[1] in the filtrate from the cobalt by acidifying the solution with hydrochloric acid in order to decompose the nitrite. Precipitate the black nickel hydroxide by adding caustic potash and bromine as just indicated for cobalt.[2] The dark brown precipitate of $Ni(OH)_3$ is reduced to the metallic state in a Rose's crucible as described for cobalt. The precipitate may also be ignited in an ordinary crucible, and weighed as nickel oxide—NiO.[3]

The potassium nitrite process is by no means perfect, since nickel can be afterwards detected with the cobalt, and cobalt with the nickel. The error in the determination of the cobalt is, however, almost balanced by the slight solubility of the potassium cobaltinitrite precipitate in the mother liquid. The precipitate should not be allowed to stand much over the 24 hours without attention. This process, as indicated above (and also Liebig's cyanide process), breaks down if alkaline earths be present.

§ 197. The Separation of Nickel—Liebig's Cyanide Process.

This process is based on the fact that nickel hydroxide alone is precipitated by bromine from an alkaline solution containing an excess of potassium cyanide. The nickel probably occurs in solution as a double cyanide of nickel and potassium, whereas the cobalt occurs in solution as potassium cobalticyanide. Bromine reacts with the former, not with the latter.[4]

The solution of the mixed sulphides is neutralised with potassium hydroxide, and treated with a solution of "pure" potassium cyanide until the precipitate first formed redissolves; add more potassium cyanide—in all, 3 or 4 grms. usually suffice. Then about 5 grms. of potassium hydroxide are added, and about 5 c.c. of bromine, with constant stirring, until the nickel is all precipitated. If necessary, add more potash in order to keep the solution alkaline throughout the whole process, or the precipitation will not be complete. The nickel should all be precipitated in about an hour. Dilute with about 800 c.c. of cold water, and determine the nickel as indicated above.[5]

The cobalt remaining in the filtrate as potassium cobalticyanide is evaporated with dilute sulphuric acid in a platinum dish on a water bath; then add concentrated sulphuric acid, and evaporate on a sand bath until dense white fumes are evolved and effervescence has ceased. This shows that the colourless cobalticyanide is all changed to rose-red cobalt sulphate. Cool. Dissolve the residue in water, and precipitate the cobalt with bromine in alkaline solution as indicated above.

In special cases, certain other methods for the determination of cobalt and nickel are useful. If suitable apparatus be available, the electrolytic methods of separation are splendid. The following are also useful in special cases.

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[1] The electrolytic process, page 394, may be used, and in fact is strongly recommended, if convenient.

[2] If the bromine be omitted, the apple-green precipitate of nickel hydroxide—$Ni(OH)_2$—is difficult to filter and to wash from alkali.

[3] It is very difficult to wash the precipitate free from alkali. The oxide can be washed with water, dried and weighed Silica can be determined as indicated in the text for cobalt, or the solution can be treated with ammonium sulphide and the precipitate ignited and weighed as NiO or metal.

[4] J. von Liebig, *Liebig's Ann.*, 65. 244, 1848; 87. 128, 1853; F. Wöhler, *ib.*, 70. 256, 1849; F. Gauhe, *Zeit. anal. Chem.*, 5. 75, 1866; C. Krauss, *ib.*, 30. 227, 1891; *Chem. News*, 63. 254, 264, 280, 293, 1891; W. Gibbs, *ib.*, 11. 125, 1865; *Amer. J. Science* (2), 39. 58, 1865.

[5] Or use the electrolytic process, page 394, which gives better results than the process indicated in the text.

§ 198. The Separation of Small Amounts of Cobalt from Large Amounts of Nickel—Ilinsky and Knorre's Nitroso-β-naphthol Process.

This process[1] depends on the fact that a solution of nitroso-β-naphthol precipitates cobalt from a mixed solution of cobalt and nickel. The reagent is so sensitive that a visible turbidity is produced in solutions which give no sign of cobalt by the nitrite process. The precipitate is rather bulky, so that the process is most convenient for separating small quantities of cobalt from comparatively large amounts of nickel.

Add a little sulphuric acid to the solution of the mixed sulphides indicated above, and evaporate the solution on a sand bath until white fumes of sulphuric acid are evolved. Cool. Dilute. Add 5 c.c. of concentrated hydrochloric acid, and then a hot acetic acid solution of freshly prepared nitroso-β-naphthol[2] as long as a precipitate of cobalti-nitroso-β-naphthol is produced. Let the voluminous precipitate settle. Test the clear solution with more reagent to find if the precipitation is complete. Let the mixture stand overnight. Filter. Wash with cold water, then with a hot 12 per cent. solution of hydrochloric acid so as to remove the nickel salt, which is soluble in hydrochloric acid. Wash with hot water until the filtrate is free from acid. Dry the precipitate and place it in a Rose's crucible. Add a little pure oxalic acid,[3] and raise the temperature gradually in order to avoid loss by spurting. Finish the ignition over a Teclu's burner. When the carbon of the filter paper is all consumed, reduce the cobalt to metal by heating in a current of hydrogen. Cool, and weigh the metallic cobalt.[4]

The greatest difficulty in this process is the elimination of carbon. The cobalt seems to form a compound with carbon which is not destroyed even by ignition over a blast. Ilinski and Knorre's reagent also precipitates copper, chromium, and iron, but it is not affected by the presence of magnesia and lime. It does not precipitate aluminium, lead, cadmium, manganese, nickel, mercury, and zinc, although these constituents may be carried down mechanically with the cobalt precipitate. The latter must then be purified by solution and reprecipitation.

§ 199. The Separation of Small Amounts of Nickel from Large Amounts of Cobalt—Brunck's α-Dimethylglyoxime Process.

If an excess of α-dimethylglyoxime be added to a strongly ammoniacal solution, containing both nickel and cobalt salts, and if the solution be boiled a short time, 1 part of nickel in the presence of 500 parts of cobalt will produce a rose coloration. When small quantities of nickel are in question, the solution should be evaporated almost to dryness.[1] This coloration is best seen when the solution is filtered and the precipitate shaken with water. Larger amounts of nickel give a scarlet red precipitate. If the precipitate be dissolved in a mixture of chloroform and alcohol, and evaporated to dryness, red needles of nickel-α-dimethylglyoxime are formed.[2] The reaction is applied quantitatively as follows:—

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[1] M. Ilinsky and G. von Knorre, *Ber.*, **18**. 699, 2728, 1885 ; **20**. 283, 1886 ; *Chem. News*, **52**. 301, 1885 ; C. Krauss, *Zeit. anal. Chem.*, **30**. 227, 1891 ; L. L. de Koninck, *Rev. Univ. Mines*, **9**. 243, 1890 ; *Chem. News*, **62**. 19, 1890 ; C. Meineke, *Zeit. angew. Chem.*, **1**. 3, 1888 ; M. Ilinsky, *Chem. Ztg.*, **19**. 1421, 1885 ; H. Copaux, *Bull. Soc. Chim.* (3), **29**. 301, 1903 ; *Chem. News*, **87**. 291, 1903.

[2] NITROSO-β-NAPHTHOL SOLUTION.—Dissolve 8 grms. of the solid in 300 c.c. of cold glacial acetic acid. Dilute with 300 c.c. of water. Filter. The solution does not keep very well. Make up a fresh solution about once a month. Nitroso-β-naphthol costs 8s. per 100 grms.

[3] If the oxalic acid be omitted, the results are usually a little high.

[4] The nickel can be determined in the filtrate by evaporating to a small bulk with sulphuric acid, and expelling most of the acid on a sand bath. The nickel may then be precipitated with caustic potash and bromine water as indicated above.

Evaporate the solution of mixed sulphides to dryness on a water bath. Dilute the residue to about 300 or 500 c.c., such that the cobalt is less concentrated than 0·1 grm. per 100 c.c. Warm the solution to about 50°; add 0·2 grm. of dimethylglyoxime in alcoholic solution,[3] and then add about 2 grms. of sodium acetate.[4] Stir the solution thoroughly, and let it stand about half an hour. A voluminous precipitate of the nickel oxime separates.[5] Filter the solution through an asbestos-packed Gooch's crucible. Wash with warm water (50°), and dry for about an hour at 110°–120°, after which there should be no further loss on drying.[6] When cold, weigh the mass as $C_8H_{14}N_4O_4Ni$, and multiply the weight so obtained by 0·2033 to get the corresponding amount of nickel oxide, NiO. There is no danger of loss of nickel if the precipitate be heated below 250°.[7] At this temperature the salt begins to sublime undecomposed. The process can be employed for separating nickel from zinc, manganese, iron, aluminium, and chromium in ammoniacal solutions in the presence of sodium acetate. With zinc-nickel mixtures, for example, the dimethylglyoxime is destroyed by boiling the filtrate from the nickel with hydrochloric acid, and the zinc precipitated by Gibb's process.

§ 200. The Electrolytic Process for Cobalt and Nickel—Fresenius and Bergmann's Process.

Nickel and cobalt cannot be precipitated satisfactorily from solutions containing free acids, but these metals are readily precipitated from solutions of the double cyanides, double oxalates, and double sulphates, or in the presence of alkaline acetates, tartrates, citrates, etc.[1] In Fresenius and Bergmann's process,[2] which is most generally used, the double sulphate of potassium and nickel, or potassium and cobalt in ammoniacal solutions, is employed. The presence of sodium phosphate[3] or ammonium sulphate is favourable to the deposition of these metals. Cobalt deposits rather more slowly than nickel, and the results with cobalt are usually a little too high.

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[1] L. Tschugajeff, *Ber.*, **38**. 2520, 1905; K. Kraut, *Zeit. angew. Chem.*, **19**. 1793, 1906; O. Brunck, *ib.*, **20**. 834, 1844, 1907; *Chem. News*, **99**. 275, 1909; A. Ivanicki, *Stahl Eisen*, **27**. 358, 1908; H. Wdowiszewski, *ib.*, **27**. 960, 1908; **29**. 358, 1910; P. Boguluboff, *ib.*, **30**. 458, 1911; L. V. W. Spring, *Journ. Ind. Eng. Chem.*, **3**. 255, 1911; F. Ibbotson, *Chem. News*, **104**. 224, 1911; H. Pederson, *Met.*, **8**. 335, 1911; S. W. Parr and J. M. Lindgren, *Trans. Amer. Brassfounders' Assoc.*, **5**. 120, 1912. For the separation of nickel and palladium, see M. Wunder and V. Thuringer, *Ann. Chim. Anal.*, **17**. 201, 1912. Platinum is qualitatively, not quantitatively, precipitated—M. Wunder and V. Thuringer, *ib.*, **17**. 328, 1912.

[2] H. Grossmann and B. Schück (*Chem. Ztg.*, **31**. 535, 643, 911, 1907) detect nickel under similar circumstances by means of dicyanodiamidine sulphate. The process is also used quantitatively—H. Grossmann, B. Schück, and W. Heilborn (*Bull. Soc. Ind. Rouen*, **38**. 116, 125, 1910). Dicyanodiamidine costs about 5d. per 10 grms.

[3] α-DIMETHYLGLYOXIME SOLUTION.—Dissolve 0·2 grm. of α-dimethylglyoxime—$CH_3.C:NOH\ C:NOH.CH_3$—in 20 c.c. of 98 per cent. alcohol. Filter the solution if necessary. The solution will not keep very long. In 1908 dimethylglyoxime cost 12s. per 10 grms.; and in October 1911 the price had fallen to 1s. 6d. per 10 grms. Hence the cost factor of this useful process is no longer so serious as it was.

[4] The precipitate is soluble in free mineral acids. Ammonium and sodium acetates render the mineral acids inert.

[5] The solution should not have more than half its volume of the alcoholic dimethylglyoxime, or appreciable amounts of the nickeloxime may be dissolved. Otherwise an excess of the solution does no harm. Theoretically, four times as much dimethylglyoxime by weight is needed as nickel to be precipitated. A small excess suffices—say five times; but if much cobalt be present, a greater excess is needed, owing to some of the glyoxime forming a complex salt with the cobalt.

[6] P. Bogoluboff, *Stahl Eisen*, **29**. 458, 1910.

[7] The cobalt can be determined in the filtrate by evaporating it to a small bulk and proceeding as indicated above. Brunck recommends the joint determination of cobalt and nickel, direct determination of nickel, and cobalt by difference.

The Electrolyte.—Mix the given solution with 5–10 grms. of ammonium sulphate and 30–40 c.c. of concentrated ammonia for every 0·25–0·30 grm. of the nickel or cobalt sulphate or chloride[4] in the solution under investigation. Dilute the solution with distilled water until it occupies a volume of about 150 c.c.

The Electrolysis.—The solution is electrolysed at the room temperature[5] with a current density of 1·0 to 1·5 amps., and 2·8 to 3·5 volts. The electrolysis is completed in the case of nickel in about 2½ to 3 hours; and in the case of cobalt, in 5 to 6 hours.[6] Break the current; pour off the exhausted electrolyte (page 359); wash, dry, and weigh the deposit.

The deposited nickel adheres firmly to the cathode, and it has a bright silver-grey colour, sometimes closely resembling the appearance of the platinum itself. The cobalt deposit is generally brown or black in colour. It is rare to see a brilliant cobalt deposit. The results with the dark-coloured cobalt deposits are quite as satisfactory as with the bright deposits.

If too little ammonia has been used in the electrolyte, some nickel may be deposited on the anode, giving low results. Too much ammonia retards the deposition of the metals. The presence of ammonium chloride or ammonium nitrate also retards the deposition of the metals.[7]

A couple of test experiments quoted from Fresenius and Bergmann's paper show that good results can be obtained. This agrees with general experience.

	Nickel.	Cobalt.	
Used	0·1233	0·1280	grm.
Found	0·1233	0·1286	grm.

Treatment of Mixed Cobalt and Nickel Sulphides.—In actual analyses, mixed cobalt and nickel sulphides are often obtained. To prepare these for analysis, ignite the filter paper in the usual manner (page 390). Dissolve the sulphides and ash of the paper in hydrochloric acid with a little nitric acid. Evaporate the solution to dryness on a water bath. Dissolve the residue in a little dilute sulphuric acid, and transfer the solution to the platinum basin for electrolysis; add 5 grms. of ammonium sulphate, 40–60 c.c. of ammonia; dilute the solution to about 150 c.c. with distilled water; and proceed with the electrolysis as indicated in the text. Weigh the mixed deposit as metallic "cobalt + nickel." Dissolve the metals in hot nitric acid, and determine either the nickel or the cobalt by one of the processes described in this work. The other metal can be obtained by difference.

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[1] W. Gibbs, *Zeit. anal. Chem.*, **3.** 336, 1864; **11.** 10, 1872; **22.** 558, 1883; F. Wrightson, *ib.*, **15.** 300, 1876; T. Schweder, *ib.*, **16.** 344, 1877; W. Ohl, *ib.*, **18.** 523, 1899; C. Luckow, *Dingler's Journ.*, **177.** 235, 1850.

[2] H. Fresenius and F. Bergmann, *Zeit. anal. Chem.*, **19.** 314, 1880.

[3] M. S. Cheney and E. S. Richards, *Amer. J. Science* (3), **14.** 178, 1877.

[4] Nitrates should be absent. If nitrates be present in the solution, evaporate to dryness with sulphuric acid in order to expel the nitric acid.

[5] If the solution is electrolysed at, say, 45°–50°, 1½ to 2 hours are needed for the electrolysis.

[6] To test for the end of the electrolysis in a colourless solution, transfer about 1 c.c. by means of a pipette to a test tube. Add H_2S water. A brown coloration will show whether the metal is all deposited. Yellow ammonium sulphide is not so good for making the test, because its yellow colour may mask the colour produced by small quantities of nickel or cobalt.

[7] If the electrolysis of ammoniacal solutions be too protracted, the cathode increases in weight as soon as all the nickel is deposited, possibly owing to the dissolution of the anode—F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2.** 115, 1911.

Removal of the Deposit from the Electrode.—Nickel is difficult to remove from the cathode, because it is inclined to become "passive." Warm nitric or sulphuric acid may be used for dissolving the metal. Owing to the close resemblance between the deposited nickel and the platinum, special care must be taken to dissolve off all the nickel before the cathode is heated ready for the next determination. It is very difficult to remove the stain left on platinum when it has been heated in contact with nickel. The removal of cobalt presents no particular difficulty, since it does not assume the passive condition, and it is readily soluble in concentrated nitric acid.

§ 201. The Colorimetric Determination of Small Quantities of Cobalt.

Lampadius' attempt[1] to determine small quantities of cobalt from the reddish-brown colour produced when ammonia is added to the solution of a cobalt salt was not very successful. The colour changes on exposure to the air.[2] Müller used a colorimeter for estimating the amount of cobalt. This measured the cobalt in terms of the intensity of the colour of solutions of its salts;[3] and Winkler, recognising that the colour of cobalt solutions is complementary to that of nickel solutions,[4] and that the one solution therefore neutralises the tint of the other, found that the maximum decolorisation occurred when the proportion of nickel was to cobalt as 3 : 1. Hence Winkler proposed adding nickel or cobalt to a given solution until the maximum decolorisation occurred. This furnished data sufficient to compute an approximation to the amount of nickel and of cobalt in a given solution. The process is not very reliable.

Skey,[5] as indicated on page 385, found that, when solutions of cobalt thiocyanate are shaken up with ether or alcohol, a blue superincumbent layer is obtained, and this reaction is sometimes inaptly called "Vogel's test" for cobalt. Skey suggested shaking out the solution of cobalt thiocyanate with ether as a means of separating cobalt and nickel; and this idea was later employed by Rosenheim and Huldschinsky,[6] and recommended for separating cobalt and nickel by a process similar to that employed by Rothe (page 456) for separation of iron.

Skey further showed that the blue colour is destroyed by sodium thiosulphate, sodium acetate, and mercuric chloride. The red colour of ferric thiocyanate, if present, masks the blue colour of the cobalt thiocyanate, and, in consequence, the iron must be removed. Wolff[1] proposed removing the iron by first adding an excess of ammonium thiocyanate, and then neutral sodium carbonate until the blood-red colour of the ferric thiocyanate disappeared. The precipitated ferric oxide was removed by filtration, and the filtrate shaken with ether to get the cobalt-blue coloration. This is quite satisfactory. Bettink preferred reducing the ferric iron to the ferrous condition by means of sodium thiosulphate until the red colour of the ferric thiocyanate disappeared. The filtered solution was then treated with ether as before. There are several objections to the use of sodium thiosulphate. These reactions can be applied to the colorimetric determination of small quantities of cobalt[2] in the following manner:—

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[1] W. A. Lampadius, *Journ. prakt. Chem.* (1), **13**. 385, 1838.

[2] T. Bodemann, *Anleitung zur Berg- und Hüttenmännischen Probierkunst*, Clausthal, 456, 1857.

[3] A. Müller, *Das complementar Colorimeter*, Chemnitz, 1854; *Journ. prakt. Chem.* (1), **60**. 474, 1853; F. Dehms, *Zeit. anal. Chem.*, **3**. 218, 494, 1864.

[4] R. Wagener, *Journ. prakt. Chem.* (1), **61**. 129, 1854; C. Winkler, *ib.* (1), **97**. 414, 1866; R. W. Challinor, *Journ. Roy. Soc. N.S.W.*, **38**. 406, 1905; E. J. Maumené, *Compt. Rend.*, **30**. 209, 1850; J. H. Gladstone, *Phil. Mag.* (4), **9**. 535, 1855; T. Bayley, *ib.* (5), **6**. 15, 1878; *Journ. Chem. Soc.*, **37**. 828, 1880; J. Bottomley, *Proc. Manchester Lit. Phil. Soc.*, **19**. 164, 1880; *Chem. News*, **42**. 56, 1880; M. Knieder, *Berg. Hütt. Ztg.*, **53**. 243, 1894; F. Dehms, *Dingler's Journ.*, **172**. 440, 1864; **173**. 436, 1864.

[5] W. Skey, *Chem. News*, **16**. 201, 1867; H. W. Vogel, *Ber.*, **8**. 1533, 1875; **12**. 2314, 1879; *Zeit. anal. Chem.*, **21**. 563, 1882; T. T. Morrell, *ib.*, **16**. 251, 1877; *Pharm. Centr.*, **17**. 394, 1877; W. H. Bettink, *Nederl. Tijdschr. Pharm.*, **11**. 43, 1899. H. Ditz (*Chem. Ztg.*, **25**. 109, 1901) studied the changes of colour of cobalt salts by the action of glycerine, ether, alcohol, acetone, etc. Skey isolated blue acicular crystals from the ethereal solution of cobalt thiocyanate. F. P. Treadwell (*Zeit. anorg. Chem.*, **26**. 108, 1901) later represented the composition of the crystals by the formula $(NH_4)_2Co(SCN)_4$.

[6] A. Rosenheim and E. Huldschinsky, *Zeit. anal. Chem.*, **40**. 809, 1901; *Ber.*, **34**. 2050, 1901; A. Rosenheim and A. Cohn, *ib.*, **33**. 1111, 1900; F. W. Dootson, *Proc. Cambridge Phil. Soc.*, **12**. 125, 1903.

Standard Solution.—Pipette 1 c.c. of standard solution of cobalt sulphate[3] into a graduated Nessler's tube,[4] 25 to 30 c.c. capacity. Add 1 c.c. of dilute sulphuric acid; 5 c.c. of water; 0·2 grm. of solid ammonium thiocyanate;[5] and water up to the 10-c.c. mark.

Test Solution.—Add 1 grm. of ammonium thiocyanate per 50 c.c. of the solution under investigation,[6] and then add concentrated sodium carbonate—Na_2CO_3—until the red colour of the ferric thiocyanate disappears.[7] Filter and wash. Neutralise the filtrate with dilute sulphuric acid, and make the solution up to 100 c.c. Pipette, say, 5 c.c. into a Nessler's tube; add 1 c.c. of dilute sulphuric acid; and make the solution up to the 10-c.c. mark with water.

The Comparison.—Fill both tubes up to the 20-c.c. mark with a mixture of ether and alcohol.[8] Shake the mixture. As soon as the ethereal and aqueous layers have separated, compare the colour of the ethereal solutions, and note if more or less standard solution is needed to make the tints of the two solutions the same. Add a diluted solution (say 1 in 10 c.c.) of the standard cobalt solution to the paler-tinted solution from a burette reading to $\frac{1}{50}$ c.c., and an equivalent amount of water to the other solution, until the tints of the two solutions are the same. Or make up other standard solutions, if necessary, containing more or less standard cobalt sulphate, until the tints of the standard and test solutions are the same. The calculations are then made in the usual manner.

EXAMPLE.—Suppose 5 c.c. of the "filter press water" of a pottery be evaporated to dryness and the residue washed, and the solution, about 5 c.c., be treated as described in the text. After a comparison, etc., the test solution was the paler. It required 2·58 c.c. of diluted cobalt sulphate (10 c.c. of standard was made up to 100 c.c. with water) to bring the tints the same. Hence the standard solution had 0·000002 grm. of cobalt, and the test solution $x+0·00000258$ grm. of cobalt. Hence $x=0·00000742$ grm. of cobalt per 5 c.c. of filter press water. But $0·00000742 \times 2·204 = 0·00001635$ grm. cobalt chloride, $CoCl_2$, per 5 c.c.; 0·00033 grm. per litre; or the equivalent of 0·00054 oz. of anhydrous cobalt chloride was escaping per gallon of the filter press water.

The aqueous layer retains about one-tenth of its volume of ether, and also a trace of cobalt; but since the standard and test solutions are similar, the error is negligibly small. Otherwise the ethereal solutions would have to be removed and the aqueous layer washed out with ether, and the two solutions compared in any convenient way.

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[1] C. H. Wolff, *Zeit. anal. Chem.*, **18**. 38, 1879; C. Zimmermann, *ib.*, **20**. 414, 1881; *Liebig's Ann.*, **199**. 1, 1879; W. H. Bettink, *Nederl. Tijdschr. Pharm.*, **11**. 64, 1899.

[2] J. W. Mellor, *Trans. Eng. Cer. Soc.*, **8**. 132, 1908.

[3] STANDARD SOLUTION OF COBALT SULPHATE.—Dissolve 0·01 grm. of cobalt in dilute sulphuric acid and make the solution up to a litre with water. This furnishes a solution containing 0·01 grm. cobalt per 1000 c.c., or 1 c.c. is equivalent to 0·00001 grm. of cobalt.

[4] The Nessler's cylinders are about 17 cm. high and 13 mm. internal diameter, and made from colourless glass. The cylinders should be as nearly alike as possible, and stoppered. See page 85.

[5] All the reagents must be free from iron—see page 200.

[6] Say, a solution obtained during the analysis of a "stained body or glaze."

[7] If no iron is present, the treatment with sodium carbonate is unnecessary.

[8] ETHER-ALCOHOL MIXTURE.—Methylated ether, 5 vols.; isoamyl alcohol, 5 vols. No naked flame should be near the bench when ether is being used.

This method is useful for estimating the small amounts of "cobalt" employed for "bleaching" china clays, pottery bodies, etc.[1]

§ 202. The Evaluation of Cobalt and Nickel Oxides.

The standard for commercial "black oxide" of cobalt is 70 per cent. of metallic cobalt, corresponding with 89 per cent. of cobalt monoxide—CoO; but it generally contains the equivalent of 71 to 72 per cent. metallic cobalt. The standard for "prepared oxide" is 74·5 per cent. of metal, corresponding with 94·6 per cent of CoO; but commercial samples sometimes run as high as 76 to 77 per cent. of metallic cobalt. This corresponds with 96 to 98 per cent. of cobalt oxide—CoO. Hence, in evaluating these oxides, a determination of the percentage of cobalt or nickel as metal generally suffices.[2] A qualitative test should always be made. If any of the metals indicated below be absent, the process can be abbreviated accordingly.

Assume, in the extreme case, that the oxide contains silica, some metals in the hydrogen sulphide group, iron, aluminium, manganese, zinc, nickel, and cobalt. In evaluating the oxide, therefore, everything is got into solution and the impurities are removed, step by step. For a full analysis, the method indicated in the schemes, pages 319 and 387, may be used; for the cobalt and nickel oxides alone, proceed as described below.

1. *Dissolution of the Oxide.*—Digest half a gram of the oxide in a 200-c.c. flask with 10 c.c. of concentrated hydrochloric acid. Filter and wash. Fuse the dried and ignited insoluble residue with sodium carbonate; take up the mass with hydrochloric acid; evaporate the mixed solutions to dryness.

2. *Removal of Silica, Iron, and Aluminium.*—Add 35 c.c. of concentrated ammonia and ammonium chloride, and warm the mixture until the residue is disintegrated; filter; wash with hot water; rinse the residue on the filter paper back into the flask; pour hot dilute hydrochloric acid (1 : 2) through the filter paper to dissolve the precipitate, collecting the runnings in the flask under the funnel; wash; boil until solution is complete; add ammonium chloride and excess of ammonia to the boiling solution; filter; wash thoroughly with hot water; and unite the two filtrates.[3]

3. *Precipitation of Copper by Hydrogen Sulphide.*—Boil off any excess of ammonia; just acidify the solution with hydrochloric acid; and then add 5 c.c. of the acid in excess; boil a few minutes; dilute to about 250 c.c. with water; pass hydrogen sulphide to precipitate copper, lead, etc. Filter, and wash with water saturated with hydrogen sulphide; and boil the filtrate to expel the hydrogen sulphide.

4. *Removal of Manganese.*—Add a slight excess of ammonia; acidify the solution strongly with acetic acid; add 1 to 2 grms. of ammonium acetate; heat the solution to 70° or 80°; saturate the solution with hydrogen sulphide; filter, and wash with hot water. The manganese remains in solution; the cobalt, zinc, and nickel are precipitated. The filtrate probably still contains

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[1] For the colorimetric determination of nickel by the use of potassium thiocarbonate, see M. Lucas, *Bull. Soc. Chim.* (3), **21**. 432, 1899; *Chem. News*, **80**. 39, 1899.

[2] For the analysis of cobalt ores, see H. Copaux, *Bull. Soc. Chim.* (3), **29**. 301, 1903; and for the analysis of nickel ores, A. Hollard, *Ann. Chim. Anal.*, 8. 401, 1903.

[3] The amount of iron and alumina is usually too small for the result to be affected by the adsorption of salts of nickel and cobalt by the precipitated iron; if otherwise, use the basic acetate separation.

traces of cobalt and nickel. To precipitate these, concentrate the solution by evaporation; add colourless ammonium sulphide; acidify the solution with acetic acid; warm; and filter, if necessary, into a separate beaker. Test the filtrate in the same way; and, if necessary, repeat the operation.

5. *Removal of Zinc.*—Wash the precipitated sulphides from the paper as completely as possible; dry, and burn the paper; dissolve everything in hydrochloric acid with a little nitric acid. The solution contains cobalt, nickel, and zinc. To remove the latter, add 2 or 3 grms. of finely crystalline ammonium chloride;[1] evaporate the solution to dryness on a water bath; heat the solid mass until all the ammonium chloride is expelled. Zinc is volatilised at the same time. When cold, dissolve the mass in aqua regia and evaporate to dryness. The solution is now ready for the separation of cobalt and nickel as described on pages 389 *et seq.*

Smalt or zaffre may be fused with sodium carbonate and sodium nitrite (page 461), or broken down by treatment with acids. The silica can be separated by evaporation of the hydrochloric acid solution (page 167), and the filtrate treated as described above for the separation of iron, or by the basic acetate process (page 362). Nickel, cobalt, bismuth, iron, lead, and arsenic, as well as silica, alumina, alkalies, and alkaline earths, may be present. The matt blues rich in alumina are best fused with potassium bisulphate, or pyrosulphate. Zinc, phosphoric and arsenic oxides, as well as cobalt, nickel, silica, etc., may here be present.

§ 203. The Volumetric Determination of Cobalt and Nickel.

The methods which have been suggested up to the present for the determination of cobalt volumetrically are not satisfactory except under special conditions, and hence no volumetric method for cobalt[2] has won a place in general practice. Volumetric methods for nickel also fail in the presence of cobalt, although the cyanide process for nickel[3] is quite good when cobalt is absent, or only present in minute quantities, and when copper, silver, gold, and metals of the platinum group are absent.

Theory of the Cyanide Process.—The cyanide process, suggested by Moore and by Campbell and Andrews, depends on the fact that, if potassium cyanide be added to a feebly ammoniacal solution of a nickel salt, a double cyanide is formed, say,

$$NiCl_2 + 4KCN = 2KCl + Ni(CN)_2.2KCN ;$$

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[1] R. Fresenius (*Zeit. anal. Chem.*, **21.** 229, 1881) says that 5 grms. of ammonium chloride suffice for 0·2 grm. of zinc oxide.

[2] C. Winkler (*Zeit. anal. Chem.*, **3.** 420, 1864) titrates with potassium permanganate in the presence of mercuric oxide. H. B. Harris (*Journ. Amer. Chem. Soc.*, **20.** 173, 1898) obtained fair results with hot dilute solutions, not with concentrated solutions. N. M'Culloch (*Chem. News*, **59.** 51, 1889) titrates cobalt cyanide with potassium bichromate after the addition of Mohr's salt. E. Fleischer (*Journ. prakt. Chem.* (2), **110.** 48, 1870) precipitates the cobalt with alkali hypochlorite, adds an excess of Mohr's salt, and titrates back with potassium permanganate. E. Donath (*Ber.*, **12.** 1868, 1879; *Chem. News*, **41.** 15, 1880) oxidises the cobalt by means of iodine in an alkaline solution, and distils the Co_2O_3 with hydrochloric acid into a solution of potassium iodide, and titrates the liberated iodine with thiosulphate. M. A. van Reis and F. Wiggart (*Zeit. angew. Chem.*, **3.** 695, 1890) boils the cobaltous salt with zinc emulsion; adds an excess of potassium permanganate, and titrates back with a solution of Mohr's salt. C. Rössler, *Liebig's Ann.*, **200.** 323, 1880; E. Rupp and F. Pfennig, *Chem. Ztg.*, **34.** 322, 1910; G. S. Jamieson, *Journ. Amer. Chem. Soc.*, **32.** 757, 1910.

[3] T. Moore, *Chem. News*, **59.** 160, 292, 1889; **72.** 92, 1895; H. Brearley and H. Jervis, *ib.*, **78.** 177, 196, 1898; E. D. Campbell and W. H. Andrews, *Journ. Amer. Chem. Soc.*, **17.** 125, 1895; E. D. Campbell and W. Arthur, *ib.*, **30.** 1116, 1908; *Chem. News*, **98.** 38, 1908; G. W. Sargent, *ib.*, **21.** 854, 1899; C. M. Johnson, *ib.*, **29.** 1201, 1907; H. Grossmann, *Chem. Ztg.*, **32.** 1223, 1908; H. Grossmann and B. Schück, *Zeit. anal. Chem.*, **47.** 169, 1908; G. Raulin, *Monit. Scient.*, **74.** 84, 1911.

and if the solution contains a little silver iodide (or a mixture of silver nitrate and potassium iodide) the solution will remain turbid until enough potassium cyanide has been added to transform all the nickel to the double cyanide. Further additions of potassium cyanide dissolve the silver iodide to a clear solution. Thus,

$$AgI + 2KCN = AgCN.KCN + KI.$$

When the silver iodide is all dissolved, it will be obvious that the transformation of the nickel to the double cyanide is completed. Hence, the potassium cyanide used in the titration represents the amount of potassium cyanide used for the formation of the double cyanide, and for the dissolution of the silver iodide. If the amount of the potassium cyanide required for the dissolution of the silver iodide be known, the amount required for the transformation of the nickel can be found by subtraction.

The Determination.—Add 2 c.c. of concentrated sulphuric acid to the solution under investigation. Neutralise the solution with ammonia.[1] Add 20 c.c. of $2N\text{-}NH_3$ to the neutral solution, and then 2 c.c. of a 2 per cent. solution of potassium iodide, and 5 c.c. of a solution of silver nitrate (5·85 grms. per litre).[2] The solution will now be turbid owing to the presence of silver iodide. Titrate[3] the cold solution with a standard solution of potassium cyanide[4] until the solution is clear, showing that all the silver iodide is dissolved. A black background is best for the titration. Add more silver iodide, so as to make the solution turbid again. Again titrate with the potassium cyanide drop by drop until the last drop clears up the opalescence. The temperature of the solution should not exceed 20°, or disturbing side reactions may set in.

Example.—Suppose it be found that 31 c.c. of the potassium cyanide solution are needed for the whole titration; that 1 c.c. of the potassium cyanide solution represents 0·0037 grm. NiO; suppose 3 c.c. of silver nitrate are needed to reproduce the turbidity the second time, and that 1 c.c. of the silver nitrate solution represents $\frac{1}{3}$ c.c. of the potassium cyanide solution. In all, $5+3=8$ c.c. of silver nitrate has been added, and this corresponds with $\frac{1}{3}\times 8 = 2{\cdot}7$ c.c. of the potassium cyanide. Hence the nickel corresponds with 31 less $2{\cdot}7 = 28{\cdot}3$ c.c. of potassium cyanide, or $28{\cdot}3 \times 0{\cdot}0037$, *i.e.* 0·105 grm. of NiO in the given solution.

Influence of Foreign Substances.[5]—Free alkalies, alkaline earths, alkaline carbonates, chlorides, bromides, phosphates, have no marked effect. If not present in excessive amounts, chromates, manganese, cobalt, arsenic, bismuth, molybdenum, tin, lead, and uranium have no marked effect. With manganese the indication is not quite so sharp or delicate. The manganese may be prevented from precipitating during the titration by the addition of ammonium chloride. For lead, use ammonium nitrate instead of sulphate, as indicated, page 336. If arsenic and antimony be present, use a little tartaric acid. Arsenic and tin should be oxidised with a little nitric acid and bromine water, and the excess boiled off.

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[1] The ammonium sulphate so formed makes the indicator more sensitive. If barium, or elements which form insoluble sulphates, be present, use nitrates or chlorides, not sulphates.

[2] Since 1 grm. of silver nitrate corresponds with 0·76 grm. of potassium cyanide, 1 c.c. of the silver nitrate, containing the equivalent of 0·008 grm. of silver iodide, will require 0·00445 grm. of potassium cyanide, or 0·345 c.c. of the solution of potassium cyanide described below. The silver nitrate should be standardised by a blank experiment without nickel. Find how many cubic centimetres of the standard solution of potassium cyanide are required to dissolve the silver iodide corresponding with 1 c.c. of silver nitrate solution. Do not trust to the calculation.

[3] In some cases, *e.g.* in the presence of manganese, if the titration be left partly completed, a precipitate may separate. This interferes with the result later on. Hence, the titration should be completed without delay. The ammonium sulphate retards the formation of the precipitate.

[4] Standard Potassium Cyanide.—Make 12·9 grms. of potassium cyanide and 5 grms. of potassium hydroxide up to a litre. The potassium hydroxide makes the solution more stable. The cyanide can be standardised by dissolving 0·08 grm. of nickel in sulphuric acid, or 0·539 grm. of nickel ammonium sulphate in water, and proceeding with the solution as described above. The cyanide should be freed from sulphur. This is sometimes effected by agitating the solution with lead monoxide, or bismuth oxide.

[5] H. Brearley and F. Ibbotson, *The Analysis of Steel Works Materials*, London, 139, 183, 1902; C. M. Johnson, *Journ. Amer. Chem. Soc.*, 29. 1201, 1907.

The results with iron, aluminium, chromium, and zinc are low. This is due to the precipitate[1] carrying down some nickel. If, therefore, these elements can be kept in solution, the titration is satisfactory. The chromium should be oxidised to chromate. Moore recommends the use of sodium pyrophosphate for keeping the zinc, iron, and aluminium in solution; while Brearley and Ibbotson recommend tartaric or citric acids to minimise the chances of error. Brearley and Ibbotson accordingly recommend the following procedure when iron and manganese have not been separated:—Add 3 grms. of citric acid and 2 grms. of ammonium sulphate per gram of sample. Add enough ammonia to make the solution feebly but distinctly alkaline. Add 2 c.c. of a 2 per cent. solution of potassium iodide, and silver nitrate until the turbidity is apparent. Titrate with potassium cyanide until the turbidity disappears. The alkaline citrate solution, containing iron in solution, is dark-coloured, and the changes are not easy to distinguish. Hence, a strong beam of light should be sent across the solution. Fig. 139 shows Lupp's arrangement, useful for titrations which require strong illumination to distinguish the end point. The light is focussed in the body of the liquid from a reflecting mirror.[2]

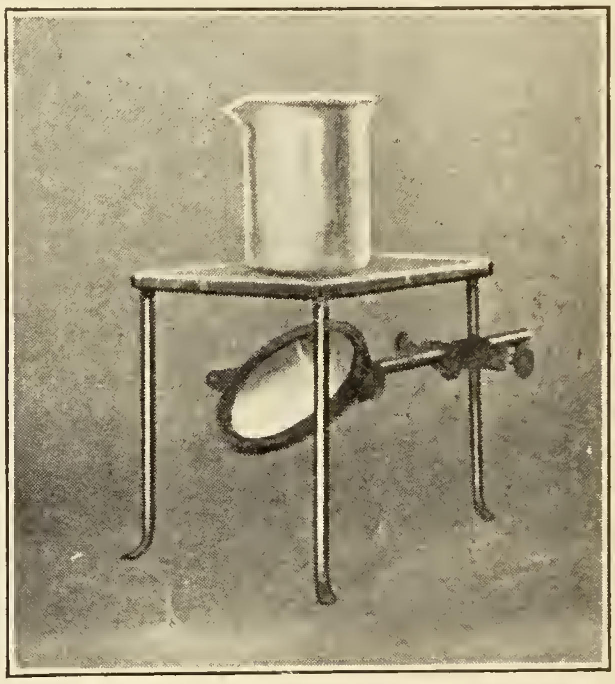
FIG. 139.—Illumination of turbid solutions during titration.

If chromium be present, the turbidity disappears before the formation of the double nickel potassium cyanide is completed, but it soon returns. The phenomena of appearance and disappearance of the turbidity recur a number of times, and it is difficult to decide just when the reaction is at an end. Hence, Johnson[3] prefers to use 12 grms. of citric acid instead of 3 grms. Johnson's plan then enables him to say that the titration can be accomplished "at almost the full speed of the burette."

If zinc be present, proceed as for iron and aluminium, but make the solution alkaline with sodium carbonate instead of ammonia. Copper should be removed by the thiocyanate process (page 350): acidify the solution with nitric acid and proceed as described above. If the amount of the other interfering elements—cobalt, silver, gold, etc.—be known, an allowance can be made; otherwise, the result of the titration gives nickel plus cobalt, silver, gold, and platinum, if these be present. Cobalt darkens the solution, owing to the oxidation of the cobaltocyanide to cobalticyanide. If the amount of cobalt be less than 10 per cent. of the total nickel, the sum Ni + Co can be determined by the titration, and the cobalt determined separately. Or the nickel can be precipitated with dicyandiamide or dimethylglyoxime; dissolved in warm dilute hydrochloric acid; and the ammoniacal solution titrated as described above.

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[1] H. Brearley, *Chem. News*, 74. 16, 1896; G. T. Dougherty, *Iron Age*, 79. 1274, 1907.

[2] A. Lupp, *Zeit. anal. Chem.*, 34. 182, 1895.

[3] C. M. Johnson, *Rapid Methods for the Chemical Analysis of Special Steels*, New York, 105, 1909.

PART IV.

SPECIAL METHODS—BASES.

CHAPTER XXX.

THE DETERMINATION OF MOLYBDENUM, TUNGSTEN, NIOBIUM, AND TANTALUM.

§ 204. Molybdenum, Tungsten, Niobium, and Tantalum in Silicate Analyses.

THE "opening up" of minerals containing tungsten, molybdenum, niobium, and tantalum[1] follows the lines indicated in different parts of this work (pages 164 and 266). First the acids—alone or mixed[2]—are tried. If these be impotent, the fluxes—sodium peroxide,[3] potassium hydroxide, potassium bisulphate or pyrosulphate,[4] etc.—are tried. Potassium hydroxide (or carbonate) is recommended as a general flux for the minerals containing the elements discussed in this chapter. The reason will appear later.

The oxides of these elements form soluble salts when fused with an excess of potassium carbonate or hydroxide. When the aqueous solution is treated with a slight excess of hydrochloric acid, a certain amount of the oxides separates, and if more acid be present, the soluble salts are decomposed, and the separation of the oxides is often practically complete.

In silicate analyses, therefore, the oxides of these elements may be found with the silica when the acid solution is evaporated to dryness.[5] If tungsten be the only member of this series present, the problem resolves into the separation of silica from tungsten oxide. Some molybdenum, if present, will separate with the silica as silicomolybdate. Niobium, tantalum, antimony,[6] tin,[7] arsenic,[8] and phosphorus,[9] if present, may also be associated with the silica. Niobium, by the way, is often called columbium and symbolised Cb.

In dealing with complex mixtures of this type, it is generally best to extract the sodium or potassium carbonate fusion with water. The aqueous solutions may contain one or more of the following: alkaline tungstate, molybdate, stannate, sulphate, aluminate, chloride, fluoride, arsenate, phosphate, antimoniate, chromate, vanadate, niobate, tantalate, silicate, etc., provided certain combinations which form insoluble precipitates are absent. The residue may contain alkaline zirconate, ferric oxide, calcium, barium, and strontium carbonates, etc.

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[1] For tantalum in clays, see A. Terreil, *Compt. Rend.*, **51**. 94, 1860.

[2] For hydrochloric acid and aqua regia, see H. Bartonec, *Oestr. Chem. Ztg.*, **12**. 114, 1909. H. W. Hutchin and F. J. Fouks (*Trans. Inst. Min. Met.*, **18**. 425, 1909) recommend boiling alkaline hydroxide (25 per cent. solution).

[3] *E.g.* W. Hempel (*Zeit. anorg. Chem.*, **3**. 193, 1895) decomposed wolframite in a few minutes by heating with four times its weight of sodium peroxide.

[4] *E.g.*, H. Cremer, *Eng. Min. Journ.*, **59**. 345, 1895.

[5] Molybdic oxide is soluble in an excess of acid.

[6] Antimony oxychloride.

[7] Stannic chloride gives a yellow precipitate with alkaline tungstates.

[8] Tin or tungsten arseniate.

[9] Tin or tungsten phosphate; and phosphomolybdates.

The treatment for the separation of the different combinations revealed by a qualitative analysis may be based on the processes indicated in this work.

§ 205. The Detection of Tungsten, Tantalum, Molybdenum, and Niobium.

Fuse, say, half a gram[1] of the finely powdered mineral with six times its weight of potassium hydroxide in a silver or nickel crucible. Extract the cold mass with hot water. Treat the filtered solution with 25 c.c. of hydrochloric acid (sp. gr. 1·16). Boil the solution, and filter. The residue may contain niobium, tantalum, tin, tungsten, silica, molybdenum, and antimony. Digest the moist precipitate with yellow ammonium sulphide. Molybdenum, tin, tungsten, and antimony dissolve; niobium and tantalum remain.

The ammoniacal sulphide solution containing molybdenum, tin, tungsten, and antimony is acidified with hydrochloric acid and boiled; digest the washed precipitate with a little hydrochloric acid and a little nitric acid; filter and wash. The precipitate contains sulphur and tungsten, if present. Treat the solution with a few pieces of metallic zinc. Antimony and tin[2] are precipitated, molybdenum and zinc remain in solution. If the solution is blue, molybdenum is probably present.

Molybdenum.—Evaporate the solution along with a little nitric acid to dryness. Dissolve the residue in ammonia. (1) Pour a portion of the solution into moderately concentrated hydrochloric acid, add a few drops of a solution of potassium thiocyanate; if no red colour develops, iron is absent. Place a little metallic zinc in the acid solution; the development of a carmine-red colour indicates the presence of molybdenum.[3] (2) Another portion of the solution is heated with a few drops of sulphuric acid on the lid of a platinum crucible until it begins to fume. When cold, an ultramarine blue colour will develop, when the acid is brought in contact with a little alcohol, if molybdenum be present.[4]

Tungsten.—(1) The residue of tungsten and sulphur indicated above, or tungstic oxide itself, gives a blue solution when digested with a little zinc in the presence of hydrochloric or sulphuric acid. (2) Stannous chloride gives a yellow precipitate with a soluble tungstate;[5] if the solution be acidified with hydrochloric acid and boiled, a blue colour is formed. (3) *Defaçqz's test.*[6] Heat a mixture of the oxide with four or five times its weight of potassium bisulphate and a few drops of sulphuric acid in a platinum capsule. Add enough sulphuric acid to prevent the mixture solidifying when it cools. On cooling, add a drop of this solution to a drop of phenol; if tungsten be present, an intense red colour is developed; if hydroquinone be used in place of phenol, an amethyst-violet coloration is formed with concentrated solutions, and a rose colour with dilute solutions.[1] Titanium and vanadium interfere with the test.

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[1] More than this is sometimes required, say, 5 grms., but only if small quantities of these elements are present. P. Nicolardot, *Compt. Rend.*, **144**. 859, 1907.

[2] Note, if arsenic and antimony be present, poisonous hydrides may be evolved. For the recognition of tin and antimony, see any of the Text-books on Qualitative Analysis.

[3] The blood-red tint with ferric salts is destroyed by the addition of phosphoric acid. This is not the case with molybdenum—R. Fresenius, *Qualitative Chemical Analysis*, London, 185, 1897.

[4] In the event of antimony or tin being present with the molybdenum, the mixture should be evaporated to dryness with phosphoric acid before it is treated with the sulphuric acid—R. Fresenius, *Qualitative Chemical Analysis*, London, 185, 1897. For the sulphuric acid test, see H. Schönn, *Zeit. anal. Chem.*, **8**. 379, 1869; O. Maschke, *ib.*, **12**. 383, 1873; *Arch. Pharm.* (3), **6**. 125, 1874; F. von Kobell, *Zeit. anal. Chem.*, **14**. 317, 1874; *Charakteristik der Mineralien*, Nuremberg, 109, 1831; *Grundzüge der Mineralogie*, Nuremberg, 284, 1838.

[5] Fuse the residual oxide with an excess of sodium carbonate, and take the mass up with water to get a soluble sodium tungstate.

[6] E. Defaçqz (*Compt. Rend.*, **123**. 308, 1896; *Chem. News*, **74**. 88, 1896) claims that this reaction will indicate the presence of between 0·0000025 and 0·000002 grm. of tungsten, whereas the blue colour developed by zinc and hydrochloric acid will only detect 0·001 grm.

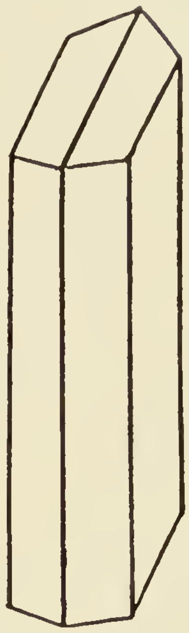
FIG. 140.—Potassium fluotantalate—K_2TaF_7.

Niobium and Tantalum.—Digest the insoluble residue,[2] indicated above, in a platinum capsule with a little hydrofluoric acid in slight excess; add a saturated solution of potassium fluoride. Evaporate the solution to a very small volume. Let the solution cool slowly. If acicular rhombic crystals of potassium fluotantalate (fig. 140) separate, tantalum is present; if plates of potassium-niobium oxyfluoride separate (fig. 141), niobium is also present. A good hand lens is a convenient means of recognising the crystals if they are small. It must be added that isomorphous potassium fluotantalate, K_2TaF_7, and potassium fluoniobate, K_2NbF_7, separate from concentrated solutions of hydrofluoric acid;[3] and if an excess of hydrofluoric acid be not present, the solution containing niobium alone furnishes the plates of oxyniobate, $K_2NbOF_5.H_2O$. By boiling dilute aqueous solutions of both salts hydrolysis occurs, and tantalum and niobium oxyfluorides are formed. The latter is much more soluble than the former, so that the appearance of a turbidity when dilute aqueous solutions of the two salts are boiled enables small traces of tantalum to be detected in the presence of niobium.

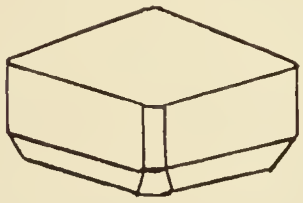
FIG. 141.—Potassium-niobium oxyfluoride —$K_2NbOF_5.H_2O$.

Pick out a few of the acicular crystals and heat them on the lid of a platinum crucible with concentrated sulphuric acid (sp. gr. 1·29) until the acid fumes strongly, so as to drive off the hydrofluoric acid. Treat the cold mass with an excess of water in a small glass capsule, and boil the solution so as to precipitate the tantalic oxide. The precipitate dissolves in an excess of hydrochloric acid, giving an opalescent solution. Metallic zinc along with hydrochloric acid does not colour the solution; tannic acid with a drop of the solution gives a light brown precipitate if tantalum be present.[4] If a few of the crystalline plates of potassium fluoniobate or potassium niobium oxyfluoride be treated in a similar manner, and the precipitate dissolved in sulphuric acid, metallic zinc will give a blue coloration;[5] and tannic acid, an orange-red coloration.[6]

§ 206. The Determination of Tungsten as Tungsten Trioxide.

If the substance under investigation can be decomposed by an acid,[7] tungsten trioxide—WO_3—will remain as an insoluble yellow powder. Repeated evaporation of a soluble tungstate (say, three times) with nitric acid or hydrochloric acid, washing, and baking at 110° to 120° will render the tungstic oxide insoluble in acids. The dry mass is moistened with concentrated nitric acid, and after a 15 minutes' digestion add, say, 20 c.c. of a hot 5 per cent. solution of ammonium nitrate. Filter.[1] Wash with the 5 per cent. ammonium nitrate solution acidified with a few drops of concentrated nitric acid until all the alkali is removed. Dry. The filter paper must be ignited separately to avoid reduction; hence, transfer the powder to a watch-glass, and ignite the filter paper in a weighed porcelain crucible, then transfer the powder carefully from the watch-glass to the crucible, and ignite until the greenish tinge passes to a clear yellow. If the green colour persists, add a couple of drops of concentrated nitric acid, and repeat the ignition.[2] Weigh the ignited mass as tungstic oxide —WO_3.

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[1] For quinine and strychnine, see F. Scheibler, *Journ. prakt. Chem.* (1), **80**. 204, 1860.

[2] Antimony can be detected in the residue by fusion with potassium cyanide. Wash. Digest the insoluble matter with hydrochloric acid (and a crystal of potassium chlorate). The antimony passes into solution. The washed residue is treated as described in the text.

[3] The form of the crystals is also modified by the nature of the mother liquid, and the temperature of crystallisation—C. Marignac, *Bibl. Univ. Arch. Genève*, **23**. 249, 1865; *ib.*, **26**. 89, 1866; *Œuvres Complètes*, Genève, **2**. 258, 334, 1894.

[4] Tungstic oxide under similar conditions gives a brown precipitate with tannic acid.

[5] See above for a blue coloration with tungstic acid under similar conditions.

[6] Molybdic acid gives an orange-red coloration with tannic acid—M. E. Pozzi-Escot, *Compt. Rend.*, **138**. 200, 1904; vanadic acid, a blue coloration—C. Matignon, *ib.*, **138**. 82, 1904.

[7] K. W. Scheele, 1781—*Opuscula Chemica et Physica*, Lipsiæ, **2**. 119, 1789—used nitric or hydrochloric acids; F. Margueritte (*Ann. Chim. Phys.* (3), **17**. 475, 1846), dilute sulphuric

Unlike the corresponding molybdenum oxide, this oxide can be calcined at the highest temperature of a Bunsen's burner without fear of appreciable loss by volatilisation. If the ignition be conducted over a blast, a 20 minutes' ignition is said to have caused a loss of about 7 per cent. Thus, tungstic oxide weighing 0·3007 grm. was reduced after 20 minutes' blasting to 0·2872 grm.[3]

§ 207. The Gravimetric Determination of Tungsten—Berzelius' Process.

A concentrated alkaline solution of the tungstate is neutralised with nitric acid, and a few drops of nitric acid in excess are added. The solution is therefore feebly acid. Add an excess of mercurous nitrate[4] solution. Agitate the solution. Then add ammonia, drop by drop, with constant stirring,[5] until a brown precipitate separates. Heat the solution to boiling. Let the precipitate settle. Filter and wash with water containing 2 per cent. of mercurous nitrate. Dry, ignite, and weigh the residual tungstic oxide as WO_3.[6]

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acid. R. Hermann, *Zeit. anal. Chem.*, **51**. 736, 1912; C. Scheibler, *Journ. prakt. Chem.* (1), **83**. 273, 1861; *Chem. News*, **6**. 182, 1862. See J. W. Mallet, *ib.*, **31**. 276, 1877, for the solubility of tungstic acid when an excess of concentrated hydrochloric acid is added to an alkali tungstate.

[1] A Gooch's crucible can be used if the precipitate is not to be subjected to further treatment.

[2] If the alkalies have not all been removed in the washing, the green tinge cannot be always removed by this treatment.

[3] H. L. Wells and F. J. Metzger, *Journ. Amer. Chem. Soc.*, **23**. 356, 1901.

[4] MERCUROUS NITRATE SOLUTION.—Digest 60 grms. of pure mercury with 25 c.c. of nitric acid (sp. gr. 1·4) and 75 c.c. of water on a water bath for about 1½ hours. Let the mixture stand overnight. Dilute the solution to 400 c.c. ($\frac{3}{4}$E). The addition of about 20 c.c. usually suffices for the precipitation. The solution should give no residue when evaporated to dryness and the mercurous nitrate volatilised.

[5] Some prefer to add the mercurous nitrate solution directly to the alkaline solution.. O. F. von Pfordten (*Liebig's Ann.*, **222**. 152, 1883; *Chem. News*, **50**. 18, 1884; *Zeit. anal. Chem.*, **24**. 92, 1885) says the mercurous nitrate may be added to the neutral solution if it is free from carbon dioxide.

[6] J. J. Berzelius, *Schweigger's Journ.*, **16**. 476, 1816; W. W. Hutchin, *Analyst*, **36**. 398, 1911; E. Bagley and H. Brearley, *Chem. News*, **82**. 270, 1900; L. Desvergnes, *Ann. Chim. Anal.*, **9**. 321, 1904; W. Gibbs, *Amer. Chem. Journ.*, **1**. 219, 1879; H. W. Hutchin and F. J. Fouks, *Inst. Min. Met.*, **18**. 425, 1909. Instead of mercurous nitrate, lead acetate is sometimes used—*e.g.* T. M. Chatard, *Amer. J. Science* (3), **1**. 416, 1871; *Chem. News*, **24**. 175, 1871; F. A. Bernoulli, *Pogg. Ann.*, **111**. 573, 1860; *Chem. News*, **5**. 116, 1862; H. H. Brearley, *ib.*, **79**. 64, 1899; F. Ibbotson and H. Brearley, *ib.*, **80**. 293, 1899; E. Zettnor, *ib.*, **16**. 12, 1867; J. S. de Benneville, *Journ. Amer. Chem. Soc.*, **19**. 377, 1897. Other organic precipitating agents have been recommended, *e.g.* quinine acetate or sulphate (J. Lefort, *Journ. Pharm. Chim.* (3), **4**. 221, 326, 1881; *Chem. News*, **45**. 57, 1882); cinchonine (H. Cremer, *Eng. Min. Journ.*, **59**. 345, 1895); benzidine (G. von Knorre, *Ber.*, **38**. 783, 1905; *Zeit. anal. Chem.*, **47**. 37, 1908; *Stahl Eisen*, **28**. 984, 1908; H. Wdowiszewski, *Chem. Ztg.*, **34**. 1365,

§ 208. The Separation of Tungsten and Silica.

Hydrofluoric Acid Process.—This is best effected by the volatilisation of the silica—in the usual manner—by treatment of the mixture with sulphuric and hydrofluoric acids (page 169). Prolonged ignition is not always sufficient to drive off the last traces of sulphuric acid. In that case, a piece of pure solid ammonium carbonate in the crucible will remove the acid in question.[1] Wells and Metzger[2] have shown that Herting's assertion[3] that some tungstic oxide is volatilised by this treatment is unfounded. The mixture, however, should not be blasted, for the reason indicated above.

Ammonia Process.—The method[4] of separating tungstic oxide from silica based on the solubility of moist tungstic oxide in ammonia is not to be used if it can be avoided, since the silicic acid is slightly soluble in the same menstruum (page 172); but the error is relatively small. If the mixture be baked, so as to reduce the solubility of the silica, some of the tungstic oxide also becomes insoluble.

Potassium Bisulphate Process.—The methods[5] of separation depending upon the fusion of tungstic oxide and silica with, say, 5 parts of potassium bisulphate, and subsequent digestion of the residue with ammonium carbonate or ammonium sulphide, $(NH_4)_2S$,[6] to dissolve the tungstic oxide, take no account of the slight solubility of silica in potassium bisulphate (page 186), and of the failure of these menstrua to dissolve all the tungstic oxide.[7] The errors are small, and the experimental results, at present, meet commercial requirements.

§ 209. The Separation of Tungsten and Tin.

Rose and Rammelsberg's Process.—Rose[8] has shown that stannic oxide may be removed from tungstic oxide by repeated ignition with ammonium chloride. The ammonium chloride reacts with stannic oxide, forming a volatile stannic chloride, while the tungstic oxide remains behind. Rammelsberg[9] recommends the following method of conducting the operation:—Mix the weighed residue from the hydrofluoric acid treatment with six to eight times its weight of ammonium chloride.[10] Place the covered crucible containing the mixed stannic and tungstic

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1910; F. W. Hinrichsen, *Mitt. König. Materialprüf. Gross. Lichter. West.*, **25**. 308, 1907)—also used for the separation of tungsten from phosphoric acid; and α-naphthylamine (M. Tschilikin, *Ber.*, **42**. 1302, 1909). B. Mdivani (*Bull. Soc. Chim.* (4), **9**. 122, 1911), precipitates W_2O_5 by adding a solution of stannous chloride to a soluble tungstate.

[1] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 343, 1851.

[2] H. L. Wells and F. J. Metzger, *Journ. Amer. Chem. Soc.*, **23**. 356, 1901; *Chem. News*, **83**. 3, 1901; A. G. McKenna, *Proc. Eng. Soc. Pennsylvania*, **16**. 119, 1900; *Eng. Min. Journ.*, **66**. 607, 1898.

[3] O. Herting, *Zeit. angew. Chem.*, **14**. 165, 1901; *Chem. News*, **84**. 75, 1901.

[4] H. Bornträger, *Zeit. anal. Chem.*, **39**. 361, 1900; J. Preusser, *ib.*, **28**. 173, 1889; *Chem. News*, **60**. 37, 1889; S. Kern, *ib.*, **35**. 67, 1877; J. Parry and J. J. Morgan, *ib.*, **67**. 260, 1893; A. Cobenzl, *Monats. Chem.*, **2**. 259, 1881; J. S. de Benneville, *Journ. Amer. Chem. Soc.*, **19**. 377, 1891; H. Cremer, *Eng. Min. Journ.*, **59**. 345, 1895; H. F. Watts, *Chem. News*, **95**. 19, 1907; L. and G. Campredon, *Ann. Chim. Anal.*, **9**. 41, 1904; L. Wolter, *Chem. Ztg.*, **34**. 2, 1910; R. Namias, *Stahl Eisen*, **11**. 757, 1891.

[5] L. Schneider and F. Lipp, *Zeit. anal. Chem.*, **24**. 292, 1885; *Chem. News*, **51**. 297, 1885; R. Schöffel, *ib.*, **41**. 31, 1880; *Ber.*, **12**. 1866, 1879; O. Herting, *Zeit. angew. Chem.*, **14**. 165, 1901; C. Marignac, *Ann. Chim. Phys.* (4), **3**. 6, 1843.

[6] H. Rose, *Pogg. Ann*, **100**. 146, 1857.

[7] R. D. Hall, *Journ. Amer. Chem. Soc.*, **26**. 1235, 1904; E. F. Smith, *Proc. Amer. Chem. Soc.*, **44**. 151, 1905.

[8] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 352, 1871; W. P. Dexter, *Pogg. Ann.*, **92**. 335, 1854.

[9] C. Rammelsberg, *Pogg. Ann.*, **120**. 66, 1864; *Chem. News*, **9**. 25, 1864.

[10] The ammonium chloride must be tested to make sure that it yields no non-volatile constituents when heated in a platinum dish.

oxides in a larger crucible. The latter is covered with a lid. Heat the crucibles as long as vapours of ammonium chloride issue from the outer crucible. Repeat the treatment three times. The object of using two crucibles is to prevent the formation of a coat of stannic oxide on the outside of the smaller crucible. The stannic oxide is formed by a reaction between the vapours of stannic chloride which issue from the crucible and the moisture of the air. The contents of the inner crucible become green and finally almost black in colour. The yellow colour is restored when the small crucible is ignited while exposed to the air. If a fourth treatment with ammonium chloride gives the same weight as the third, it is assumed that all the stannic oxide has been driven off. The inner crucible is then ignited alone and finally weighed as indicated in § 206, page 408. The following numbers, by Rammelsberg himself, illustrate the accuracy of the process:—

Stannic oxide taken	0·6977	0·554 grm.
Tungstic oxide taken	0·7335	1·332 grm.
Tungstic oxide found	0·7255	1·337 grm.

Donath and Müller's Process.—According to Rammelsberg,[1] Rose's method of reduction by heating a mixture of tin and tungsten oxides in a current of hydrogen, and dissolving out the reduced tin with hydrochloric acid, is not very exact.[2] Donath and Müller[3] obtained better results by mixing the two oxides with twice their weight of zinc dust, and, after 15 minutes' ignition in a covered crucible, dissolving out the tin by boiling with dilute hydrochloric acid (1 : 2). Add sufficient potassium chlorate to the cold solution to oxidise the blue tungsten oxide to the yellow oxide. Dilute the solution with 1·5 times its volume of water, and after 24 hours, filter, ignite, and weigh the precipitate as WO_3. The tin can be determined in the filtrate by precipitation with hydrogen sulphide, etc.

§ 210. The Separation of Tungsten from Tin and Antimony—Talbot's Process.

The two processes which precede will sometimes remove any antimony which may be present, but Hallopeau[4] has shown that when a mixture of soluble antimony and tungsten salts is treated with mercurous nitrate, a mercurous antimonio-tungstate—$3HgSbO_3 . 2WO_3$—is precipitated, and this, on ignition, furnishes antimony tetroxide and tungsten trioxide. The separation, according to Hallopeau, is best effected by Talbot's process for the separation of tungsten and tin.[5]

In Talbot's process[6] the mixed oxides[7] are fused with potassium cyanide as indicated on page 269. If too little potassium cyanide be employed, a black residue containing tungsten may be formed. One part of the mixed oxides with

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[1] C. Rammelsberg, *Pogg. Ann.*, **120**. 66, 1864 ; *Chem. News*, **9**. 25, 1864.

[2] For reduction by hydrogen between 600° and 900°, forming either a lower oxide or metal, see C. Marignac, *Ann. Chim. Phys.* (4), **3**. 9, 1864 ; E. Defaçqz, *Compt. Rend.*, **146**. 1319, 1908 ; **144**. 848, 1907 ; C. Friedheim, W. H. Henderson, and A. Pinagel, *Zeit. anorg. Chem.*, **45**. 396, 1905. The process is recommended for the separation of tungstic oxide and silica by L. E. Rivot, *Ann. Chim. Phys.* (3), **30**. 188, 1850 ; A. Hilger and H. Haas, *Ber.*, **23**. 458, 1890.

[3] E. Donath and F. Müller, *Monats. Chem.*, 8. 647, 1887 ; *Chem. News*, **59**. 73, 1889 ; E. Donath, *Zeit. angew. Chem.*, **19**. 473, 1906 ; H. Angenot, *ib.*, **19**. 956, 1906 ; J. Preusser, *Zeit. anal. Chem.*, **28**. 173, 1889.

[4] L. A. Hallopeau, *Bull. Soc. Chim.* (3), **17**. 170, 1897.

[5] Hallopeau found that the fusion of the mixture of antimony and tungsten oxides with sodium hydroxide and extraction of the sodium tungstate with alcohol is not satisfactory. Some sodium antimoniate passed into solution.

[6] J. H. Talbot, *Amer. J. Science* (2), **50**. 244, 1870 ; *Chem. News*, **22**. 229, 1870 ; R. Helmhacker, *Eng. Min. Journ.*, **60**. 153, 1896 ; B. Setlik, *Chem. Ztg.*, **13**. 1474, 1889 ; *Chem. News*, **61**. 54, 1890 ; E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**. 239, 1897.

[7] Tin and tungsten ; antimony and tungsten ; or tin, antimony, and tungsten.

12 parts by weight of potassium cyanide usually suffices. The tin and antimony remain behind as metals; the alkaline tungstate formed at the same time passes into solution when the mass is leached with water. Filter and wash. The aqueous solution is boiled with an excess of nitric acid[1] to drive off the volatile cyanogen compounds. The tungstate is then precipitated by the usual process. If phosphorus be present, it will be found in the solution with the tungsten. The separation is described below. The metallic bead is dissolved in acid, and analysed in the ordinary manner—mixture of tin and antimony.[2]

§ 211. The Separation of Tungsten from Arsenic and Phosphorus—Kehrmann's Process.

The separation of arsenic and tungsten is exceedingly difficult, because part of the arsenic is retained very tenaciously by the tungsten as a complex salt. The distillation process for separating arsenic and tungsten does not give satisfactory results.[3] The following process is due to Kehrmann.[4] The same process can be applied, *mutatis mutandis*, to the separation of tungsten and phosphorus.

Fuse between 1 and 2 grms. of the sample with twice as much sodium hydroxide as is required to combine with the arsenic oxide. Add enough water to dissolve the resulting cake. Boil the solution in an Erlenmeyer's flask for about half an hour. Cool. Add three times as much ammonium chloride as is needed to form chlorides with the alkalies present. Add ammonia—about one-fourth the volume of the solution under investigation—and cold magnesia mixture. In about 12 hours the precipitate of ammonium magnesium arsenate is filtered and washed with a solution of ammonia and ammonium nitrate (page 285). It is advisable to dissolve the precipitate in dilute acid, repeat the precipitation a number of times,[5] and treat the precipitate as indicated on page 285.

The tungstic acid is separated from the combined filtrates by evaporation with nitric acid (page 408). The precipitate is washed with a mixture of nitric acid and ammonium nitrate, and weighed as indicated on page 408. It is difficult to get the tungsten quite free from magnesia. Gooch[6] first determines the total weight of tungsten and arsenic, then separates the tungsten by mercurous nitrate process, and estimates the arsenic by difference.

§ 212. The Precipitation of Molybdenum as Sulphide.

Molybdenum is precipitated from an acid solution as sulphide—MoS_2—in the hydrogen sulphide group along with copper, etc. It is almost impossible to effect complete separation in a hydrochloric acid solution. The separation is more complete in sulphuric acid solutions, but even then the separation is not satisfactory in a reasonable time. For instance, a solution of ammonium molybdate acidified with five volumes of concentrated sulphuric acid was saturated with hydrogen sulphide. The solution was filtered after it had been allowed to settle for an hour, and the filtrate was again treated with hydrogen sulphide. This sequence of operations was repeated in all five times. A little molybdenum sulphide was precipitated each time. Hence, *molybdenum, in acid solutions, is but imperfectly precipitated by hydrogen sulphide at atmospheric pressures.*[1]

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[1] Note the poisonous fumes of the cyanogen compounds which are evolved render it necessary to perform the operation under a hood.

[2] If any antimony adheres tenaciously to the walls of the crucible, remove the metal by treatment with acids; or, if antimony or tin alone be present, wash the crucible, dry and weigh. Add some ammonium chloride, and heat the crucible to redness; the antimony volatilises. The loss in weight represents the amount of metal which adhered to the crucible.

[3] C. Friedheim and P. Michaelis, *Ber.*, 28. 56, 1888; but see S. Hilpert and T. Dieckmann, *Ber.*, 46. 152, 1913.

[4] F. Kehrmann, *Liebig's Ann.*, 245. 56, 1888; *Ber.*, 20. 1813, 1887. F. W. Hinrichsen (*Mitt. Königl. Materialprüfungsamt.*, 28. 229, 1910), for the separation of both phosphorus (P_2O_5) and tungsten (WO_3), recommends the mercurous nitrate process (page 408); the ignited precipitate is fused with alkali carbonate. The phosphorus can be precipitated from the aqueous solution of the cold cake by first precipitating the phosphates with magnesia mixture, and after taking up the precipitate with nitric acid, reprecipitate (page 598).

[5] The arsenic and phosphorus can be separated in the usual manner if they are present together.

[6] F. A. Gooch, *Proc. Amer. Acad.*, 16. 134, 1881; *Amer. Chem. Journ.*, 1. 412, 1879; W. Gibbs, *ib.*, 7. 337, 1885; H. Bullnheimer, *Chem. Ztg.*, 24. 870, 1900; *Chem. News*, 85. 184, 1902.

If a pressure bottle be employed, the results are satisfactory. The pressure flask (page 277) of 300, 500, or 1000 c.c. capacity is closed by a ground-glass plate.[2] About 250 c.c. of the solution are placed in the flask, and saturated with hydrogen sulphide by passing a rapid stream of gas through the solution.[3] Dilute the solution to about 500 c.c. with water saturated with hydrogen sulphide. The flask is then placed in a cold water-bath and gradually heated to boiling. The bath is kept at that temperature for about an hour. Let the bottle cool; empty the contents into a beaker; and wash the bottle with dilute acid (sulphuric acid 1, water 50) saturated with hydrogen sulphide. Let the precipitate settle. Filter, and wash the precipitate with the dilute acid saturated with hydrogen sulphide.

If several members of the hydrogen sulphide group be present, the precipitated sulphides are digested with ammonium monosulphide for a couple of hours, when molybdenum, arsenic, antimony, and tin,[4] if present, will pass into solution. Vanadium and uranium, if present, are not precipitated by the above treatment. Tungsten is partly precipitated, but not if 3 to 5 grms. of tartaric acid be added to the solution before passing the hydrogen sulphide.[5] If much iron be present, an appreciable quantity may be carried down with the sulphides. For instance, a solution containing 0·1076 grm. of iron with different amounts of molybdenum in the same solution gave the following numbers:

Molybdenum . . .	0·00492	0·00984	0·02460	0·04921	grm.
Ferric oxide . . .	0·0001	0·0002	0·0003	0·0005	grm.

when the iron was separated from the precipitated molybdenum sulphide and weighed as ferric oxide. To recover iron from the molybdenum sulphide, dissolve the washed precipitate in a mixture of 10 c.c. of hydrochloric acid, 5 c.c. of nitric acid, and 10 c.c. of concentrated sulphuric acid. Evaporate the solution until copious fumes of sulphur oxides are evolved. Cool. Add 50 c.c. of water and an excess of ammonia. The ferric hydroxide which separates may be filtered off.

If no other member of the ammonium sulphide sub-group be present, the warm solution is acidified with hydrochloric or sulphuric acid, and the reddish-yellow solution is boiled to drive off the hydrogen sulphide.[6] Filter and wash the brown precipitate with hot water acidified with hydrochloric (or sulphuric) acid saturated with hydrogen sulphide. The precipitated molybdenum sulphide may now be treated in several different ways—gravimetric or volumetric.

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[1] E. Döhler, *Chem. Zeit.*, **24**. 537, 1900; *Chem. News*, **82**. 294, 1900; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 183, 1911; F. van Dyke Cruser and E. H. Miller, *Journ. Amer. Chem. Soc.*, **26**. 675, 1904; *Chem. News*, **90**. 204, 218, 1904.

[2] An empty "citrate of magnesia" bottle makes a good pressure flask for the operation.

[3] A fast current of gas causes less trouble by the sticking of the sulphide to the walls of the tube than a slow current of the gas. B. Herstein (*Bull. U.S. Dept. Agric., Chem.*, **150**. 44, 1912) uses 0·75 c.c. thioacetic acid per 0·1 grm. MoO_3 in place of hydrogen sulphide.

[4] Selenium, tellurium, and germanium, if present, will be found mainly in the ammonium sulphide solution.

[5] H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**. 358, 1871. If tungstic oxide be present, most of it will be found in the residue with the silica. The silica is driven off by means of hydrofluoric acid (page 169), and the residue is treated as indicated on page 408 for WO_3.

[6] F. E. Zenker, *Journ. prakt. Chem.* (1), **58**. 257, 1853.

Arsenic can be separated from molybdenum by the magnesia-mixture process described on page 283. Two or three precipitations are needed to obtain a precipitate of ammonium magnesium arsenate free from molybdenum.[1]

Tin sulphide can be separated by treatment with a solution of oxalic acid slightly acidified with hydrochloric acid, as indicated in Clarke's process (page 296).

§ 213. The Gravimetric Determination of Molybdenum as Oxide, and as Sulphide.

Determination of Molybdenum as Oxide.—If molybdenum alone be present, the sulphide can be conveniently transformed into the oxide by washing it first with dilute sulphuric acid (1 : 20), and finally with alcohol until all the acid is removed. The moist filter paper is placed in a large porcelain crucible and dried in an air bath. Carbonise the filter paper over a small flame while the cover is on the crucible. Remove the cover. Burn the carbon from the sides of the crucible with as small a flame as possible, and raise the temperature of the crucible very gradually. When the evolution of sulphur dioxide has ceased, cool. Add a little mercuric oxide suspended in water. Stir up the mixture in the crucible, and evaporate to dryness on the water bath. Drive off the mercuric oxide by gentle ignition.[2] Weigh as molybdenum trioxide—MoO_3. The oxide should be white, not tinted blue.

Errors.—The chief difficulties in determining molybdenum as trioxide arise from the tendency of the sulphide to oxidise so violently as to project particles from the crucible during calcination; and the tendency of the oxide to volatilise at comparatively low temperatures.[3] When the sulphide is calcined, a blue oxide is first formed. This contains less oxygen than the trioxide, and the calcination must therefore be continued until the mass in the crucible is white, not blue, when cold. This requires so prolonged a calcination that the oxide begins to volatilise before all the blue oxide is transformed into trioxide and the weight is constant. For instance, Collett and Eckardt[4] roasted the sulphide[5] at a low temperature and weighed the crucible and contents after the lapse of different intervals of time. The results are illustrated in fig. 142. The curve shows that the weight decreases rapidly as the sulphide is oxidised. Immediately after all has been converted into the trioxide (*A*, fig. 142), the oxide continues to lose weight, and after some time, about a couple of hours, the weight remains nearly constant, although the weight of the substance is really 1–2 per cent. less than it should be. This is due to the volatilisation of the oxide,[1] although the oxide in the crucible still has a blue tint. If the temperature of calcination be raised, the loss by volatilisation is greater. This is illustrated by the quick descent of the curve *CD* (fig. 142). With some practice, it is possible to conduct the operation quite satisfactorily. Collett and Eckardt, however, consider that the process should be abandoned, and the molybdenum weighed as sulphide.

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[1] Arsenic can also be separated by the distillation process indicated on page 280. In order to avoid the introduction of large amounts of iron, C. Friedheim and P. Michaelis (*Ber.*, **28.** 1414, 1895) recommend distillation from methyl alcohol saturated with hydrochloric acid.

[2] The mercuric oxide helps to burn off the carbon, and also assists in the removal of some sulphur oxide.

[3] E. Collett and M. Eckardt, *Chem. Ztg.*, **33.** 968, 1909. M. Seligsohn (*Journ. prakt. Chem.* (1), **67.** 472, 1856) fuses the sulphide with lead oxide and ammonium nitrate. The excess in weight over the amount of PbO used represents the molybdic oxide—MoO_3; E. Döhler (*Chem. Ztg.*, **24.** 537, 1900) prefers gentle ignition of the sulphide in a Rose's crucible in a current of hydrogen and weighing as MoS_2; or ignition in a current of hydrogen at a higher temperature and weighing as metal, as recommended by O. F. von Pfordten (*Ber.*, **17.** 734, 1884); W. T. Taggart and E. F. Smith (*Journ. Amer. Chem. Soc.*, **18.** 1053, 1896) recommend igniting the sulphide with oxalic acid and weighing as MoO_3; and C. Friedheim and H. Euler (*Ber.*, **28.** 2061, 1895) ignite the sulphide at a high temperature in air and weigh as MoO_3.

[4] E. Collett and M. Eckardt, *Chem. Ztg.*, **33.** 968, 1909.

[5] Similar results were obtained by calcining ammonium molybdate, and fig. 145 applies to both this salt and to the sulphide.

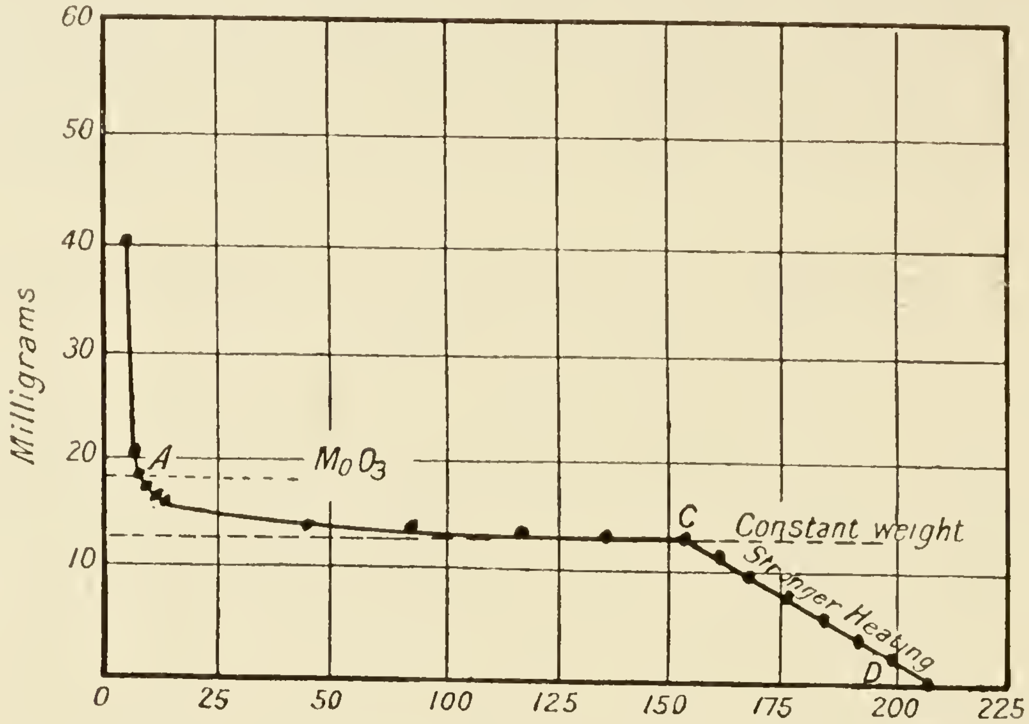

FIG. 142.—Loss in weight during the ignition of molybdenum sulphide.

Determination of Molybdenum as Sulphide.—This determination is less liable to error, and the result is rather more certain than the preceding method, but the apparatus required is a little more complex. The washed sulphide precipitate is dried; the precipitate separated from the paper, and preserved between two watch-glasses while the filter paper is burned to ash in a crucible. The sulphide is transferred to the same crucible, which is then fitted with a perforated lid (Rose's crucible, fig. 138, page 392), and the whole calcined to a constant weight in a current of hydrogen gas. The contents of the crucible are finally weighed as molybdenum sulphide—MoS_2. The equivalent weight of molybdenum trioxide is obtained by multiplying the weight of the sulphide by 0·8992.

For instance, working with a known amount of molybdenum trioxide, it was found that:

MoO_3 used	0·1413	0·1422	0·1500	grm.
MoS_2 found	0·1573	0·1578	0·1672	grm.
MoO_3 calculated from sulphide .	0·1414	0·1419	0·1503	grm.

The results are therefore quite satisfactory.

§ 214. The Gravimetric Determination of Molybdenum as Lead Molybdate.

If a gravimetric process be required for the molybdenum in soluble salts like ammonium molybdate, dissolve, say, 0·5 grm. of the salt in 200 c.c. of water and add a few drops of ammonia, followed by 2 or 3 c.c. of (33 per cent.) acetic acid,[2] and 4 or 5 grms. of ammonium chloride. Heat the solution to boiling, and while boiling add gradually, with constant stirring, 45–50 c.c. of a solution of lead acetate.[1] Boil two or three minutes more with vigorous agitation. The cream-coloured granular precipitate settles and filters rapidly. When the precipitate has settled, filter through an asbestos-packed Gooch's crucible, and wash by decantation with boiling water containing 5 grms. of ammonium chloride or ammonium acetate and five drops of acetic acid per 200 c.c. Transfer all the precipitate to the Gooch's crucible, and when the washings are free from lead, wash the precipitate twice with boiling water. Heat the crucible on an asbestos plate until dry, and then over a naked flame. Cool in a desiccator, and weigh as lead molybdate—$PbMoO_4$. Multiply the weight of the lead molybdate so obtained by 0·39236 to get the corresponding amount of MoO_3.

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[1] The sublimation of the oxide is shown by the presence of small glistening crystals above the mass in the crucible.

[2] If more acetic acid be present, some lead molybdate may be dissolved.

Errors.—If sulphates be present, as would be the case if the precipitated sulphide were dissolved in hot nitric acid, lead sulphate will be precipitated with the lead molybdate. Hence, it is necessary to roast molybdenum sulphide to oxide before it is dissolved in acid, preparatory to precipitating as lead molybdate.

Cruser and Miller give the following trials with known amounts of molybdenum:

Used . . .	0·14765	0·14793	0·17302	0·17211	0·19657	grm.
Found . . .	0·14745	0·14793	0·17301	0·17210	0·19656	grm.

Vanadium, if present, interferes with the test. According to Brearley, the presence of acetic acid, lead acetate, alkaline nitrates, chlorides, and acetates, salts of manganese, copper, cobalt, nickel, zinc, magnesium, mercury, barium, strontium, calcium, arsenic, cadmium, phosphorus, aluminium, and uranium do not interfere: silicates give slightly high results; iron and chromium should be removed, by the addition of sodium hydroxide to the boiling solution.[2]

§ 215. The Volumetric Determination of Molybdenum by Potassium Permanganate.

Dissolve the sulphide in a beaker or dish by digestion with a mixture of 10 c.c. of concentrated sulphuric acid, 10 c.c. of hydrochloric acid, and 5 c.c. of nitric acid. Evaporate[3] the solution until sulphurous fumes are evolved. Let the solution cool, and then neutralise it with ammonia, add 10 c.c. of concentrated sulphuric acid, and make the solution up to 200 c.c. When the solution has a temperature of 70°–75°, pour it through a reductor (page 191) with a column of granulated zinc[4] (20–30 mesh) about 37 or 38 cm. long. Arrange the suction so that it takes 6 minutes for the solution to pass through the reductor tube.[5]

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[1] LEAD ACETATE SOLUTION.—Dissolve 4 grms. of the salt in 100 c.c. of water.

[2] For some properties of lead molybdate, see page 331. T. M. Chatard, *Amer. J. Science* (3), **1**. 416, 1871; *Chem. News*, **24**. 175, 1871; P. Guichard, *Compt. Rend.*, **131**. 389, 419, 1900; H. Brearley, *Chem. News*, **78**. 203, 1898; **79**. 2, 14, 1899; F. Ibbotson and H. Brearley, *ib.*, **79**. 3, 1899; **81**. 269, 1900; *Analysis of Steel Works Materials*, London, 85, 273, 1902; L. Schindler, *Zeit. anal. Chem.*, **27**. 137, 1888; F. van Dyke Cruser and E. H. Miller, *Journ. Amer. Chem. Soc.*, **26**. 675, 1904.

[3] The solution is inclined to bump badly. Blowing air through the solution during the evaporation prevents this.

[4] F. Pisani, *Compt. Rend.*, **59**. 301, 1864; C. Rammelsberg, *Pogg. Ann.*, **127**. 281, 1866; A. Werneke, *Zeit. anal. Chem.*, **14**. 1, 1875; H. Bornträger, *Zeit. anal. Chem.*, **37**. 438, 1898; E. Knecht and F. W. Atack, *Analyst*, **36**. 98, 1911.

[5] There has been some discussion on the product obtained by reducing molybdic salts. Some say that Mo_2O_3 is formed (W. A. Noyes and E. D. Frohman, *Journ. Amer. Chem. Soc.*, **16**. 553, 1894); others consider that $Mo_{24}O_{37}$ is obtained (A. A. Blair and J. E. Whitfield, *Journ.*

Titrate the solution immediately with standard potassium permanganate.[1] The test experiments are excellent.

§ 216. The Separation of Tungsten and Molybdenum—Hommel's Process.

Tungsten and molybdenum can be separated by the action of warm sulphuric acid (sp. gr. 1·378) upon the moist freshly precipitated[2] oxides MoO_3 and WO_3.[3] The former passes into solution, the latter remains insoluble. Hommel says that this process only gives satisfactory results when the moist oxides are first digested with concentrated sulphuric acid, and a few drops of dilute nitric acid, say, in a porcelain dish over a naked flame for about half an hour.[4] When the solution is cold, add about three times its volume of water. Filter, wash the precipitate with dilute sulphuric acid (1 : 20), and finally wash it two or three times with alcohol, ignite as indicated on page 408, and weigh as WO_3. The molybdenum in the filtrate may be precipitated by hydrogen sulphide (page 277), or, if only small quantities are present, the solution may be evaporated to dryness and weighed in the platinum dish. Hommel's process is quite satisfactory. For example, Hommel obtained the following results with artificial mixtures of tungsten and molybdenum trioxides:

Table LVI.—Test Analyses, Tungsten and Molybdenum Mixtures.

Tungstic trioxide.		Molybdenum trioxide.	
Used.	Found.	Used.	Found.
0·9616	0·9614	0·1077	0·1080
0·8732	0·8738	0·0501	0·0503
0·7029	0·7035	0·1030	0·1028
0·5737	0·5740	0·1184	0·1180

Amer. Chem. Soc., **17**. 747, 1895); others again say that the reduction does not go so far as this. E. H. Miller and H. Frank (*ib.*, **25**. 919, 1903) did not get Mo_2O_3, in the reductor, but they could find no definite stopping place at $Mo_{24}O_{37}$, although reduction under the usual conditions proceeds very close to this. With the reductor arranged as described in the text, the iron standard of the permanganate multiplied by 0·88 gives the equivalent MoO_3 standard, and by 0·01579, the phosphorus standard. With amalgamated zinc, the factors were 0·8842 and 0·01586 respectively. If the reduction had been to $Mo_{24}O_{37}$, the factors would have been 0·8832 and 0·01584 respectively. It is best to standardise the potassium permanganate by the method of reduction with known solutions of molybdate. See page 599.

[1] STANDARD SOLUTION OF AMMONIUM MOLYBDATE.—Dissolve 6·132 grms. of ammonium molybdate—$(NH_4)_6Mo_7O_{24}.4H_2O$—in a litre of water. The solution contains the equivalent of 0·005 grm. MoO_3 per c.c. The strength of the solution may be verified by precipitation of the molybdenum as lead molybdate—page 414. The potassium permanganate solution is approximately $\frac{1}{10}$N, and it is standardised by running the standard ammonium molybdate solution through the reductor and titrating as described in the text.

[2] If the oxides have been ignited, it is best to fuse them with from four to six times their weight of sodium carbonate, dissolve the fused mass in water, evaporate the solution to dryness, and add the concentrated sulphuric and nitric acid as described in the text.

[3] E. D. Desi, *Journ. Amer. Chem. Soc*, **19**. 213, 1897; M. Rueginberg and E. F. Smith, *ib.*, **22**. 772, 1900; *Chem. News*, **83**. 5, 1901; W. Hommel, *Ueber die quantitative Trennung von Wolfram und Molybdän*, Zürich, 1902.

[4] If the solution is greenish-coloured, add a drop or two of dilute nitric acid to oxidise the tungstic oxide to yellow tungstic acid.

Rose's Tartaric Acid Process.—In Rose's method,[1] the alkaline salts under investigation are treated with an excess of sulphuric acid, and the tungsten is kept in solution by the addition of a considerable amount of tartaric acid[2] while the molybdenum is precipitated by hydrogen sulphide in a pressure flask. The tartaric acid is afterwards destroyed by repeated evaporation with nitric acid (page 208), and the tungsten finally separated in the usual manner as WO_3. Friedheim and Meyer[3] have raised the question: Is all the molybdenum precipitated in the presence of the tartaric acid? The trial results with known mixtures of molybdenum and tungsten are, however, satisfactory. The objection to the process rests on the time consumed in the destruction of the large quantities of tartaric acid.

§ 217. The Separation of Tungsten and Molybdenum—Péchard's Process.

Péchard's process[4] is based on the fact that if a weighed mixture of tungsten and molybdenum (oxides or alkaline salts) be placed in a boat, and heated between 250° and 270° in a current of dry hydrogen chloride, the molybdenum is volatilised as $MoO_3.2HCl$ and deposited in the form of long acicular white crystals in the cooler parts of the tube, while tungsten oxide remains behind in the boat.

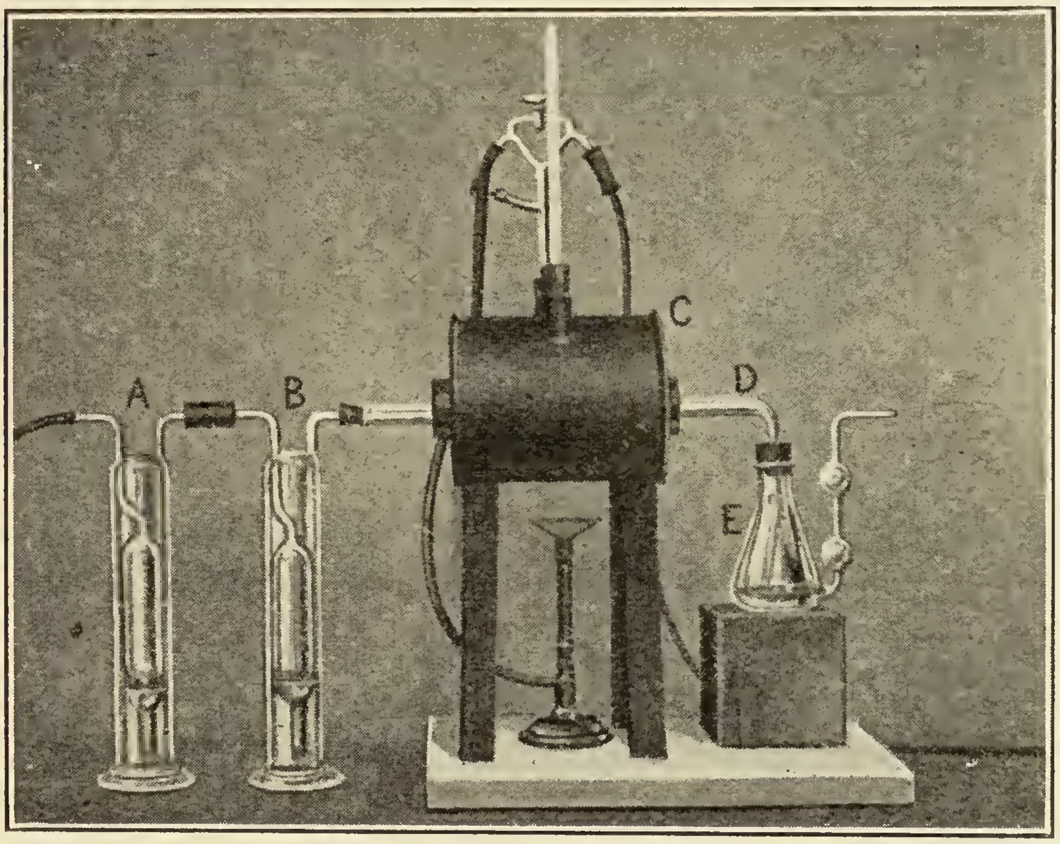

Fig. 143.—Separation of Molybdenum from Tungsten.

The Apparatus.—The arrangement indicated in fig. 143 may be employed for the purpose. A piece of wide glass tubing *D* holds a boat containing a weighed quantity of the mixed oxides. The tube is connected at one end with an apparatus for generating hydrogen chloride (fig. 125, page 281). The hydrogen chloride gas is passed through a wash-bottle *A* containing concentrated hydrochloric acid, and dried by passing through a wash-bottle *B* containing concentrated sulphuric acid. The opposite end of the tube is connected with an absorption tube *E* containing a little water.

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[1] H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, 2. 358, 1871.
[2] J. Lefort, *Ann. Chim. Phys.* (5), 9. 93, 1877.
[3] C. Friedheim and R. Meyer, *Zeit. anorg. Chem.*, 1. 76, 1892.
[4] E. Péchard, *Compt. Rend.*, 114. 173, 1891; *Zeit. anorg. Chem.*, 1. 262, 1892; *Chem. News*, 65. 89, 1892.

The Sublimation.—The tube containing the boat is heated to 270°[1] in the tube oven *C*, fitted with thermometer and thermostat. The sublimate of $MoO_3 . 2HCl$ is driven forward into the absorption tube, every now and again, by heating the part of the combustion tube *D* with a naked Bunsen flame.

The Tungstic Oxide.—When sublimation has ceased (about 1½ hour), the boat may contain tungsten oxide with or without sodium chloride, according to the nature of the substance under investigation. The sodium chloride, if present, is removed by washing the residue with water; the tungsten oxide is filtered into a weighed Gooch's crucible, ignited as indicated on page 106, and weighed as tungsten trioxide—WO_3.

The Molybdic Oxide.—The molybdic hydrochloride decomposes in contact with the water, forming a brick-red chloride—$Mo_3O_5Cl_8$—insoluble in hydrochloric acid, but readily soluble in nitric acid. The sublimate is washed from the combustion tube and from the absorption tube into an evaporating basin with water containing a little nitric acid. The solution is evaporated to dryness on a water bath; the residue is dissolved in a little ammonia; evaporated to dryness; ignited as indicated on page 413; and weighed as molybdenum trioxide—MoO_3.

The Results.—The separations by this process are excellent. For instance, with artificial mixtures:

Tungstic oxide used . .	0·2834 grm.	Molybdic oxide used . .	0·0386 grm.
Tungstic oxide found . .	0·2838 grm.	Molybdic oxide found . .	0·0380 grm.

The comparatively elaborate apparatus is considered a disadvantage in the laboratory of a works. This objection would not be serious if a large number of determinations had to be made. The time factor is then significant.[2]

§ 218. The Determination of Niobium and Tantalum—Simpson's Process.

The elements niobium and tantalum are often associated with tungsten, and, if present, they will be precipitated with the tungsten trioxide. Many tantalum minerals are free from tungsten, and since tantalum is now one of the "industrial elements," the analysis of compounds containing tantalum is sometimes required.

Opening Tantaliferous Minerals.—Several methods of opening the minerals have been suggested, and possibly some have special advantages in particular cases. Fusion with potassium bisulphate or pyrosulphate is generally recommended,[3] but the fusion is then usually very protracted—5 hours is not always sufficient for the work. The platinum crucible is much attacked by the operation, and the subsequent analysis is beset with difficulties arising from the partial solubility of the oxides under investigation in the aqueous extract of the fused cake. Fusion with potassium hydroxide[1] gives better results than potassium bisulphate. Many finely powdered minerals are decomposed by a half-hour's fusion at a dull red heat. The following process is due to Simpson.[2]

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[1] If the temperature be much greater than 270°, tungsten may sublime; if much less, the separation may be incomplete.

[2] For the separation of tungsten and vanadium, see C. Friedheim, *Ber.*, **23**. 352, 1890; *Chem. News*, **65**. 27, 1892; A. Rosenheim and C. Friedheim, *Zeit. anorg. Chem.*, **1**. 313, 1892; C. Friedheim, W. H. Henderson, and A. Pinagel, *ib.*, **45**. 396, 1905; C. Friedheim and C. Castendyck, *Ber.*, **33**. 611, 1900; W. Gibbs, *Zeit. anal. Chem.*, **23**. 543, 1884; **25**. 544, 1886; *Amer. Chem. Journ.*, **4**. 377, 1883; **5**. 378, 1883; **1**. 219, 1879; F. Mohr, *Lehrbuch der chemischen-analytischen Titrirmethode*, Braunschweig, 314, 1877; A. Šafařik, *Liebig's Ann.*, **109**. 84, 1859; C. R. von Hauer, *Ber. Wien. Akad.*, **39**. 448, 1860; A. Rosenheim, *Ber.*, **23**. 3208, 1890; P. E. Browning and R. J. Goodmann, *Zeit. anorg. Chem.*, **13**. 427, 1897; C. Reichard, *Chem. Ztg.*, **27**. 4, 1903; F. Rothenbach, *Ber.*, **23**. 3050, 1890; A. Carnot, *Compt. Rend.*, **104**. 1803, 1850, 1887; **105**. 119, 1887.

[3] W. Gibbs, *Amer. J. Science* (2), **37**. 355, 1864; W. P. Headden, *ib.* (3), **41**. 91, 1891; T. B. Osborne, *ib.* (3), **30**. 229, 1885; *Chem. News*, **53**. 43, 1886; W. B. Giles, *ib.*, **95**. 1 37, 1907; **99**. 1, 1909; L. Smith, *ib.*, **48**. 13, 29, 1883; *Amer. Chem. Journ.*, **5**. 44, 73, 1885; M. E.

Three grams[3] of pure potassium hydroxide are fused in a 4-cm. silver or nickel crucible resting on a wire gauze. When the potassium hydroxide in the crucible is in a state of tranquil fusion, remove the lid, and drop into the crucible 0·5 grm. of the finely powdered mineral.[4] Mix the contents by quickly rotating the crucible. Heat the mass to a dull red heat for 10 minutes longer; remove the lid; and again agitate the mass. Place the crucible in a hole in an asbestos pad, as described on page 266. Heat the crucible over a naked flame at a bright red heat for about half an hour. Remove the cover carefully to avoid losing the blob of flux on the under side, and let the lid cool upside down. Tilt the crucible on one side, so that the molten contents solidify on one side of the crucible.

When cool, pour 10 c.c. of dilute hydrochloric acid (sp. gr. 1·08) into a 300-c.c. beaker. Place the crucible in a beaker, and fill the crucible two-thirds with warm water. Immediately cover the beaker with a clock-glass. The action is somewhat violent, and if any spurts from the crucible it will be caught by the basin. The action will subside in a couple of minutes. Then transfer the contents of the crucible to the beaker. Wash crucible, basin, and lid with water, assisted by a "policeman," then with dilute acid, and finally with water. About 20 c.c. of acid are required for the washing, and the solution occupies from 80 to 100 c.c. Add a drop or two of alcohol to destroy the potassium manganate.

Isolation of the Tantalum and Niobium Oxides.—Boil the solution with 5 to 10 c.c. of hydrochloric acid (sp. gr. 1·1611) on a hot plate.[5] The tantalum and niobium hydroxides are precipitated. To make sure that the precipitation is complete, dilute the solution to 200 c.c. and boil 15 minutes more. Let the precipitate settle; decant the clear liquid through a 12·5-cm. close-packed filter paper. Filter and wash the residue with dilute hydrochloric acid (sp. gr. 1·0843), until the washings give no indication of iron.[6] The filtrate contains the tin, iron, magnesium, calcium, manganese, copper, nickel, and titanium. The residue contains tantalum, niobium, tungsten, silica, antimony, and some of the tin.

Pennington, *Amer. Chem. Soc. Journ.*, **18.** 38, 1896; *Chem. News*, **75.** 8, 18, 31, 38, 1897; C. Marignac, *Ann. Chim. Phys.* (4), **13.** 5, 1857; T. Prior, *Min. Mag.*, **15.** 83, 1910; W. Blomstrand, *Journ. prakt. Chem.* (1), **99.** 40, 1866; R. Hermann, *ib.* (2), **5.** 66, 1872; L. Weiss and M. Landecker, *Zeit. anorg. Chem.*, **64.** 65, 1909; *Chem. News*, **101.** 2, 13, 26, 1910; E. F. Smith, *ib.*, **92.** 209, 1905; *Proc. Amer. Phil. Soc.*, **44.** 151, 1905; R. D. Hall and E. F. Smith, *ib.*, **44.** 177, 1905; *Chem. News*, **92.** 220, 232, 242, 252, 262, 276, 1905; G. Chesneau, *Compt. Rend.*, **149.** 1132, 1910; O. Ruff and E. Schiller, *Zeit. anorg. Chem.*, **72.** 329, 1911; R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden mit der Erdsäuren*, Stuttgart, 296, 1912.

[1] Potassium in preference to sodium hydroxide because of the greater solubility of the potassium salts of the oxides under investigation.

[2] E. S. Simpson, *Bull. West Australia Geol. Sur.*, **23.** 72, 1906; *Chem. News*, **99.** 243, 1909.

[3] If but small quantities of these elements are in question, it is advisable to take as much as 30 grms. of potassium hydroxide, and 5 grms. of the mineral.

[4] Note that the proportion of mineral to flux is as 1 : 6.

[5] Less acid can be used if no titanium is present; the titanium is kept in solution by the hydrochloric acid.

[6] If the filtrate becomes turbid, it may be necessary to dilute the solution and boil for a longer period.

A small amount of the niobium may not be precipitated if much titanium be present. It seems as if "a soluble double chloride of titanium and niobium is formed, part of the niobium only being precipitated." Hence, the results for the niobium may be a little low, and the tantalum correspondingly high. In the absence of appreciable amounts of titanium,[1] it is claimed that the percentage of tantalum and niobium obtained by this method can be relied upon to be accurate to 0·1 per cent.

Removal of Tin, Antimony, Tungsten, and Silica from the Residue.—If niobium and tantalum alone be present, dry the precipitate, burn the filter paper (page 408); ignite at a bright red heat for 15 minutes, and weigh as $Nb_2O_5 + Ta_2O_5$. If tungstic acid be present, digest the moist precipitate[2] with ammonia,[3] in which tungstic oxide is soluble. Filter and wash.[4] Ignite the precipitate and weigh. The loss in weight represents the tungstic oxide. Treat the mass with sulphuric acid and hydrofluoric acid (page 169), ignite, and weigh again.[5] The loss in weight represents the silica. Place the weighed residue in a weighed porcelain boat, and heat the mixture in a current of hydrogen (page 269). The tin is reduced.[6] Digest the mixture in hydrochloric acid.[7] Ignite the washed residue, and weigh as $Nb_2O_5 + Ta_2O_5$. The loss in weight represents the tin oxide.

Determination of Tin.—The filtrate contains chloride of tin, etc. The solution is treated with hydrogen sulphide in the usual manner (page 309). The tin so obtained is added to that recovered from the first precipitate.

A nickel crucible is used for the determination of the tantalum, niobium, and tin; but for the determination of the iron, aluminium, manganese, and rare earths, etc., it is best to fuse a separate portion in a silver crucible, and reject the precipitate of tantalum, niobium, etc., and the hydrogen sulphide precipitate. The analysis is continued with the filtrate from the hydrogen sulphide precipitate.

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[1] According to L. Weiss and M. Landecker (*Zeit. anorg. Chem.*, **64**. 65, 1909; *Chem. News*, **101**. 2, 13, 26, 1910), the formation of this compound is hindered by the addition of an oxidising agent—sodium nitrate—to the alkali. After dissolving in water and filtering, very little titanium remains in solution, and this is completely precipitated by hydrogen sulphide, without carrying down the other earth acids. The titanium can also be determined colorimetrically in the mixed oxides, since the colour is not affected by niobium and tantalum—G. Chesneau, *Compt. Rend.*, **149**. 1132, 1909; C. H. Warren, *Amer. J. Science* (4), **22**. 520, 1906; *Chem. News*, **94**. 298, 1906; R. D. Hall and E. F. Smith, *Journ. Amer. Chem. Soc.*, **27**. 1369, 1905.

[2] Washed free from hydrochloric acid—test with dilute solution of silver nitrate.

[3] Some recommend digesting the moist residue with yellow ammonium sulphide to remove tin, tungsten, etc.—H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 349, 1851; F. Wöhler, *Die Mineral-Analyse in Beispielen*, 140, 1861; W. P. Headden, *Amer. J. Science* (3), **41**. 89, 1898; M. E. Pennington, *Journ. Amer. Chem. Soc.*, **18**. 38, 1896. In that case, there is a slight loss of the niobic acid if sulphates are present (W. B. Giles, *Chem. News*, **99**. 1, 1909). The reduction process offers many advantages in analysis of tin ores where small amounts of titanium, niobium, and tantalum have to be separated from large amounts of tin—A. Hilger and H. Haas, *Ber.*, **23**. 458, 1890. See also R. D. Hall, *Journ. Amer. Chem. Soc.*, **26**. 1235, 1904; E. F. Smith, *Proc. Amer. Phil. Soc.*, **44**. 151, 1905.

[4] Some silica may then be found contaminating the tungstic oxide. The ammoniacal solution is evaporated to dryness, ignited, and weighed as $WO_3 + SiO_2$. The latter is determined by the hydrofluoric acid treatment and added to the main silica.

[5] F. D. Metzger and C. E. Taylor, *Zeit. anorg. Chem.*, **62**. 383, 1909.

[6] Simpson recommends the removal of antimony and tin by digestion with ammonium sulphide; re-fuse the residual oxides and repeat the operations.

[7] The hydrogen may be passed through a beaker of water (fig. 122) and the tin recovered. If the potassium cyanide fusion be adopted (page 269), insoluble niobic and tantalic acids may envelop the metallic tin, and protect the tin from the action of the acid later on; and some may dissolve in the potassium cyanide. The insoluble residue is digested with acids to remove tin (and antimony if present). Niobic and tantalic acids remain insoluble. The niobic and tantalic oxides dissolved in the potassium cyanide can be recovered by boiling the solution with nitric acid. The tungstic oxide is separated from the tantalic and niobic oxides by ammonia as indicated above.

§ 219. The Separation of Tantalum and Niobium—Marignac's Process.

Marignac's process[1] for the separation of tantalum and niobium is probably the best. It is based upon the different solubilities of potassium fluotantalate—K_2TaF_7—and of potassium fluoniobate—$K_2NbOF_5.H_2O$.[2] One part of the latter salt is soluble in 12–13 parts of cold water, while 1 part of potassium fluotantalate dissolves in 150–157 parts of cold water. The separation is tedious, and sometimes "not worth while"[3]—see the next section.

It is convenient to use four platinum dishes—"A" dish, 7·5 cm. in diameter; "B" dish, 9 cm.; "C" dish, 6 cm.; and "D" dish, 5 cm. in diameter—for the separation.

Fuse the (weighed) mixed oxides of niobium and tantalum in a platinum crucible with eight times their weight of potassium carbonate. When solution is complete, cool the mass. Digest the cake in water.[4] Boil the mixture with dilute hydrochloric acid to precipitate the niobic and tantalic acids. Collect the precipitate on a filter paper; wash into, say, dish "C." The filter paper, folded inside out, is placed in dish "D," covered with hot water, and a few drops of hydrofluoric acid are added. Warm the mixture on a hot plate for a few minutes. Pour the solution into dish "C." Repeat the washing of the filter paper with very dilute hydrofluoric acid, and finish by washing the paper four times with hot water.

First Crop of Crystals.—The dish "C" now contains all the niobium and tantalum oxides. Put the dish on a hot plate. If solution be not complete in a few minutes, add another drop of hydrofluoric acid, but avoid an excess of this acid. Add slowly, with constant stirring, a boiling aqueous solution of 0·7 grm. of potassium fluoride to the boiling solution in basin "C." Evaporate the contents to about 10 c.c.[5] Wash down the sides of the basin with a few drops of hot water. Cool the vessel slowly to about 15°. Decant the clear solution containing the niobium and part of the tantalum through a 7-cm. filter paper[6] into dish "B." Wash the felted mass of crystals of potassium fluotantalate four times with cold water.

Second Crop of Crystals.—Evaporate the mixed filtrate and washings down to about 5 c.c. Cool the solution slowly as before. Decant the solution through a 5·5-cm. filter paper into dish "A." Wash the crystals four times with cold water. If flat plates of potassium-niobium oxyfluoride (fig. 141) are present, wash the mass until they are removed.

Third Crop of Crystals.—Evaporate the solution to dryness on a water bath.

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[1] C. Marignac, *Ann. Chim. Phys.* (4), **8**. 5, 49, 1865; E. S. Simpson, *Bull. West Australia Geol. Sur.*, **23**. 71, 1906; A. Tighe, *Journ. Soc. Chem. Ind.*, **25**. 681, 1907; O. Ruff and E. Schiller, *Zeit. anorg. Chem.*, **72**. 329, 1911; E. Meimberg, *Zeit. angew. Chem.*, **26**. 83, 1913.

[2] Or $2KF.NbOF_5.H_2O$. G. Krüss and L. F. Nilson, *Ber.*, **20**. 1676, 1887.

[3] Commercial ores of tantalum are valued at, say, £1 per unit percentage—see page 384. The value of the ore is lessened in proportion to the amount of niobium associated with the tantalum.

[4] If any remains insoluble, filter, ignite the residue, and fuse with a little potassium carbonate. Add the aqueous extract to the main solution.

[5] It is sometimes stated that solutions of tantalum fluorides when evaporated lose tantalum fluoride with the vapour of hydrofluoric acid and steam. This seems to be an error—O. Ruff and E. Schiller, *Zeit. anorg. Chem.*, **72**. 329, 1911. No loss was detected by evaporating solutions of tantalum fluoride in sulphuric acid to dryness. Similar remarks apply to the calcination of tantalic oxide with ammonium fluoride. Potassium fluotantalate alone may be slightly volatile when heated, but Ruff and Schiller could detect no loss when potassium fluotantalate was heated up to its melting point.

[6] A rubber funnel, or a glass funnel coated with cerasine or the wax mixture of page 634, is used.

Cool, add one drop of hydrofluoric acid. Run 1 to 5 c.c.[1] water from a burette into the solution. Heat the vessel quickly to dissolve the residue. Add 0·1 grm. of potassium fluoride dissolved in 1 c.c. of water. Note the volume of the solution for "correction *a*." Cool the solution for about an hour at 15° or less; filter it into a small platinum dish; and wash three or four times with a few drops of water at 15° or less. Note the volume of the liquid used for the washing—"correction *b*."

Determination of the Niobium.[2]—Add 8 c.c. of sulphuric acid (sp. gr. 1·29) to the filtrate and washings. Evaporate the solution on a sand bath until fumes of sulphur oxides appear. Continue the heating for about 20 minutes longer in order to drive off all the fluorine compounds. See that no fluorides remain unattacked on the side of the dish out of reach of the acid. Cool. Pour the mixture into 150 c.c. of water in a 300-c.c. beaker. Wash the dish with cold water assisted by a "policeman." Boil the solution 20 minutes in order to precipitate all the niobium and tantalum. Filter, wash with boiling water, and dry. Ignite until the filter paper is burnt, add a gram of solid ammonium carbonate, cover the crucible, and re-ignite to constant weight. Weigh the dish, which contains practically all the niobium and a small amount of tantalum.

Correction for the Tantalum.—The amount of the tantalum admixed with the columbium is determined from the observation that 1 c.c. of the water, slightly acidifed with hydrofluoric acid, used in the final crystallisation dissolves the equivalent of 0·002 grm. of Ta_2O_5 (correction *a*), and 1 c.c. of water used in the final washing (correction *b*) dissolves the equivalent of 0·00091 grm. of Ta_2O_5. In illustration, suppose that 0·5 grm. of tantalite furnished 0·3819 grm. of the mixed tantalum and niobium oxides. 4 c.c. of the acidified solution (correction *a*) were in contact with the crystals of potassium fluotantalate, and 4 c.c. of water (correction *b*).

Platinum crucible plus precipitate	14·3550	grms.
Platinum crucible alone	14·3211	,,
Precipitate	0·0339	grm.
Correction *a* (0·002 × 4)	0·0080	grm.
Correction *b* (0·00091 × 4)	0·0036	,,
Total correction	0·0116	,,
Precipitate	0·0339	grm.
Correction	0·0116	,,
Niobium oxide	0·0223	,,
Mixed oxides	0·3819	,,
Tantalum oxide	0·3406	,,

Hence, the sample had 78·12 per cent. of tantalum oxide, and 4·26 per cent. of niobium oxide. It is claimed that this tedious method of separation is accurate to about 1 per cent.[3]

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[1] The amount depends upon the amount of niobium expected to be present. 1 c.c. per 0·035 grm. Nb_2O_5. Usually about 3 c.c. suffices.

[2] For a colorimetric process for estimating niobium, see E. Meimberg, *Zeit. angew. Chem.*, **26**. 83, 1913.

[3] L. Weiss and M. Landecker (*Zeit. anorg. Chem.*, **64**. 65, 1909; *Chem. News*, **101**. 2, 13, 26, 1910) conduct the analysis by fusion with potassium bisulphate; extract with hot water acidulated with sulphuric acid; add sulphurous acid to the boiling solution until the precipitate becomes flocculent; in 20–30 minutes, filter and wash with sulphurous acid. The residue, containing tantalum, niobium, titanium, and tin, is neutralised with ammonia; extracted with ammonium sulphide; heated in a platinum crucible; and fused with a mixture of sodium carbonate and nitrate. Extract with water, filter, treat with hydrogen sulphide. Filter, and precipitate the niobic and tantalic acids with sulphurous acid as before. Fuse the ignited

§ 220. The Estimation of Niobium and Tantalum Oxides—Specific Gravity Method.

The great difference between the specific gravities of tantalic oxide (8·710) and niobic oxide (4·552) has suggested methods for evaluating ores [1] and also the oxides [2] of these elements from the specific gravity of the mixture. The specific gravities of the oxides appear to become constant after blasting for an hour. The specific gravity of the mixture is not quite a linear function; an empirical table is therefore constructed, from which the specific gravity of all possible mixtures can be obtained by interpolation.

Determination of the Specific Gravity.—Foote and Langley use the ordinary specific gravity bottle with the stopper extra carefully ground. Place the unweighed powder in a small beaker half full of water. Boil the water for half an hour by passing an electric current through a fine spiral of platinum wire suspended in the water.[3] Agitate the powder frequently. Cool. Decant most of the water from the beaker. Wash the residue into the specific gravity bottle through a small funnel by means of boiled water. The bottle is filled to overflowing, and any powder or air-bubbles floating on the surface are swept off with a glass rod. Remove any air-bubbles from the sides of the bottle by means of a platinum wire. Place the bottle in a dish of water at 20° for 20 minutes. Insert the stopper. Wipe the top. Dry and weigh. Transfer the contents to a platinum dish;[4] evaporate to dryness; ignite over the blast for 5 minutes;

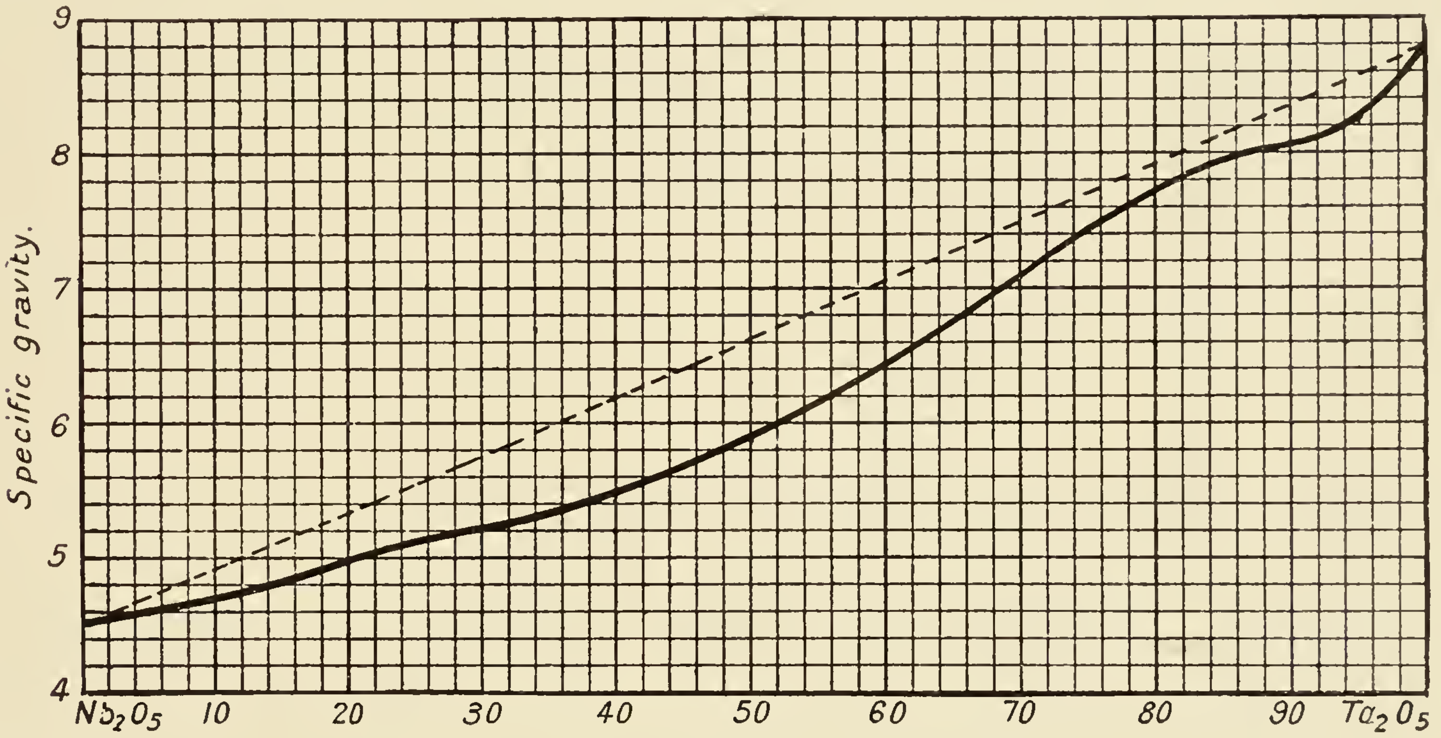

FIG. 144.—Specific gravities of mixtures of niobic and tantalic oxides (Foote and Langley).

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precipitate of mixed niobic and tantalic acids with sodium carbonate and nitrate; digest with warm water; cool; and pass carbon dioxide through the solution. Tantalic acid alone is precipitated. E. Wedekind and W. Maass, *Zeit. angew. Chem.*, **23**. 2314, 1910; O. Hauser and A. Lewite, *ib.*, **25**. 100, 1912.

[1] S. L. Penfield and W. E. Ford, *Amer. J. Science* (4), **22**. 61, 1906 (stibiotantalite); E. S. Simpson, *Bull. West Australia Geol. Soc.*, **23**. 71, 1906 (iron- and mangano-tantalites). The estimations are usually accurate to less than 5 per cent.

[2] H. W. Foote and R. W. Langley, *Amer. J. Science* (4), **30**. 393, 1910; *Chem. News*, **103**. 53, 1911.

[3] Boiling in the ordinary manner is impracticable owing to "bumping." The powder is heavy and settles rapidly.

[4] In transferring the powder to the dish, loss can be avoided by inverting the bottle over the dish (fig. 146, page 434) and shaking the bottle slightly until the powder runs out. A trace of powder sticks to the sides of the bottle. Hence, dry the bottle at 120°, and weigh. The increase in weight represents the powder in the bottle, usually not more than 0·002 grm.

and weigh. Hence calculate the specific gravity. Duplicate determinations agree to within 2·2 per cent.

Example.—Suppose the empty specific gravity bottle weighed 26·9 grms., and, after due correction, the mixed oxides weighed 6·2 grms.; the bottle, mixed oxides, and water weighed 69·8 grms.; and the bottle and water only 64·8 grms. Since

$$\text{Specific gravity} = \frac{\text{weight of mixed oxides}}{\text{weight of an equal volume of water}},$$

it follows that the weight of a volume of water equal to the volume of the mixed oxides is: $64·8 + 6·2 - 69·8 = 1·2$. Hence the required specific gravity is $6·2/1·2 = 5·17$. The corresponding percentage amounts of tantalic and niobic oxides can be read from fig. 144.

Given a mixture of two constituents A and B, of known specific gravity s_1 *and* s_2 *respectively, to find what proportion of each is present when the specific gravity of the mixture, S, is known.*

Let W denote the weight of the mixture, S its specific gravity; let x of constituent A be present, then $W - x$ of B is present. Since the weight of a substance divided by its specific gravity represents its volume, we have

$$\frac{W}{S} = \frac{x}{s_1} + \frac{W - x}{s_2}; \text{ or, } x = \frac{Ws_1(s_2 - S)}{S(s_2 - s_1)}$$

Hence, the mixture contains

$$\frac{100s_1(s_2 - S)}{S(s_2 - s_1)} \text{ per cent. of A ;}$$

$$100 - \frac{100s_1(s_2 - S)}{S(s_2 - s_1)} \text{ per cent. of B.}$$

Examples.—(1) A mixture of clay (sp. gr. 2·6) and lignite (sp. gr. 1 2) has a specific gravity 2·0: what proportions of clay and lignite are present? Here $S = 2·4$; $s_2 = 2·6$; $s_1 = 1·2$; hence, the mixture contains 7·14 per cent. of lignite and 92·86 per cent. of clay.

(2) A mixture containing tantalic and niobic oxides has a specific gravity 5·85, niobic oxide alone has a specific gravity 4·552, and tantalic oxide, 8·71: what is the percentage composition of the mixtures? *Answer*—Nearly 54 per cent. of tantalic oxide and 46 per cent. of niobic oxide.

Preparation of the Mixed Oxides.—The method of preparing the oxides should be as fixed and as definite as possible. The specific gravity of the mixed oxides becomes constant after igniting for an hour over the blast in a platinum crucible. Artificial mixtures of tantalic and niobic oxides gave specific gravities:

Tantalic oxide .	0	10	20	30	40	50	60	70	80	90	100
Specific gravity .	4·552	4·746	4·929	5·200	5·474	5·850	6·434	7·083	7·654	8·098	8·716

These numbers are plotted in fig. 144. Hence, given the specific gravity of the mixed oxides, the proportion of niobic and tantalic oxides can be determined by interpolation. The results are probably more exact than with Marignac's gravimetric process. In illustration, two determinations of tantalic and niobic oxides on a sample of niobite or columbite were made by the specific gravity and by Marignac's process:

	Specific gravity process.		Marignac's process.	
Tantalic oxide	16·54	15·81	14·43	13·60
Niobic oxide	62·23	63·23	63·68	65·75

CHAPTER XXXI.

DETERMINATION OF GOLD AND SELENIUM.

§ 221. The Precipitation of Gold and Platinum.

Gold is precipitated from cold acid solutions by hydrogen sulphide as a dark brown sulphide;[1] if the solution be hot, some metallic gold is also precipitated. The sulphide dissolves in alkali monosulphide extremely slowly, but a little more quickly in the polysulphide, and forms a brownish-red solution. If, therefore, the attempt be made to separate gold from the precipitate of mixed sulphides by ammonium or sodium monosulphide, part of the gold will be found with the tin, antimony, and arsenic; and part with the metals insoluble in alkaline sulphide.

What has here been stated with respect to gold sulphide might be repeated for platinum sulphide.[2] The solubility of platinum sulphide in ammonium or sodium monosulphide is facilitated by the presence of arsenic and other sulphides.

On account of the difficulty involved in separating gold and the platinum metals from the other members of the hydrogen sulphide group, it is best to separate these elements before precipitating the hydrogen sulphide group; or to redissolve the hydrogen sulphide precipitate in acids, and separate the gold and platinum metals from the solution of the sulphides. To separate gold, advantage is taken of the ease with which gold compounds are reduced to the metal. Several reducing agents are available: sulphurous acid,[3] oxalic acid,[4] ferrous chloride (or sulphate),[4] hydrazine hydrochloride,[5] hydroxylamine hydrochloride,[6] alkaline formaldehyde solutions,[7] alkaline hydrogen peroxide solutions,[8] chloral hydrate,[9] magnesium,[10] nickel,[11] hypophosphorous acid,[12] cane sugar,[13] etc.

Sulphurous acid, oxalic acid, and hydrazine hydrochloride are most convenient. The choice of the right precipitating agent is determined by the nature of the accompanying elements. The precipitation of gold by these reducing agents generally leads to low results. For instance, Hoffmann[1] found:

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[1] Probably AuS. A. Levol, *Ann. Chim. Phys.* (3), **30.** 356, 1850; U. Antony and A. Lucchesi, *Gazz. Chim. Ital.*, **19.** 545, 1889; **20.** 601, 1890; L. Hoffmann and G. Krüss, *Ber.*, **20.** 2369, 2704, 1887; W. Bettel, **56.** 133, 1887; J. Riban, *Bull. Soc. Chim.* (2), **28.** 241, 1877.

[2] To facilitate subsequent filtration, R. Gaze (*Apoth. Ztg.*, **27.** 959, 1912) adds a little mercuric chloride.

[3] P. Berthier, *Ann. Chim. Phys.* (3), **7.** 82, 1843.

[4] L. Hoffmann and G. Krüss, *Liebig's Ann.*, **238.** 66, 1887; *Chem. News*, **56.** 83, 1887.

[5] P. Jannasch and O. von Meyer, *Ber.*, **38.** 2129, 1905.

[6] C. Winkler, *Ber.*, **22.** 890, 1889; A. Lainer, *Monats. Chem.*, **12.** 639, 1891; P. Jannasch and O. von Meyer, *Ber.* **38.** 2129, 1905.

[7] L. Vanino, *Ber.*, **31.** 1763, 1899; *Zeit. Chem. Ind. Koll.*, **1.** 272, 1906. For formic acid, W. Bettel, *Chem. News*, **56.** 133, 1887.

[8] L. Vanino and L. Seemann, *Ber.*, **32.** 1968, 1899; *Chem. News*, **82.** 70, 1900; L. Rössler, *Zeit. anal. Chem.*, **49.** 739, 1910.

[9] P. J. Dirvell, *Bull. Soc. Chim.* (2), **46.** 806, 1886.

[10] C. Scheibler, *Ber.*, **2.** 295, 1869.

[11] V. Goldschmidt, *Zeit. anal. Chem.*, **45.** 87, 1906.

[12] F. Treubert, Dissertation, München, 1909.

[13] P. Leidler, *Zeit. Chem. Ind. Koll.*, **2.** 103, 1907.

Table LVII.—Comparison of Different Precipitating Agents for Gold.

Precipitating agent.	Used.	Found.	Per cent. loss.
Sulphurous acid	3·12360	3·11916	0·14
Sulphurous acid	2·14739	2·14688	0·03
Oxalic acid	2·15292	2·15040	0·12
Ferrous chloride	1·65596	1·65535	0·04

This loss arises from the fact that the gold is precipitated in a very fine state of subdivision, and minute particles of gold pass through the filter paper. In consequence, it is best to work with solutions as concentrated as possible, and to let the mixture stand in contact with the acid mother liquid for some time in a warm place, and agitate the solution thoroughly from time to time. This treatment favours the coagulation of the particles of gold, and thus facilitates "clean" filtrations.[2]

Precipitation by Sulphurous Acid.—The acid solution under investigation is concentrated on a water bath until crystals begin to form as a drop of the solution is cooled on the end of a glass rod. Add sufficient water to dissolve all the crystals,[3] and digest the solution for half an hour on a water bath with an excess of sulphurous acid. At the end of that time the liquid should be clear, and smell of sulphur dioxide. The addition of sulphur dioxide from time to time may be necessary. The solution is then filtered, washed with dilute hydrochloric acid, and the metallic gold ignited in a weighed porcelain crucible.

This precipitating agent is superior to both oxalic acid and ferrous chloride. There is no danger of loss by spurting, as occurs with oxalic acid, which decomposes with the formation of carbon dioxide; and the precipitated gold is more easily washed free from salts than is the case when ferrous salts are employed. The time required for complete precipitation—half an hour—is shorter than that required for complete precipitation with oxalic acid and ferrous chloride. If selenium be present, it will be precipitated with the gold. If platinum be present, and the solution be not sufficiently acid, the precipitated gold will be contaminated with platinum, and the results for gold will then be a little high. Oxalic acid, however, gives the best separations of gold from platinum, although, in separating gold from platinum, it is usual to first precipitate the latter metal as ammonium or potassium chloroplatinate. Sulphurous acid gives better separations of gold from palladium than ferrous chloride or oxalic acid, and there is little to choose between these three agents for the separation of gold from iridium, rhodium, and ruthenium.

A large excess of hydrochloric acid generally retards the precipitation of gold. Nitric acid is, of course, supposed to be absent; this is removed by repeated evaporation with hydrochloric acid.[1] No notice need be taken of any separation of gold during the evaporation.

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[1] L. Hoffmann, *Untersuchung über das Gold*, Erlangen, 11, 1887; E. Přiwoznik, *Oester. Zeit. Berg. Hütt.*, 59. 639, 1911; W. Bettel, *Chem. News*, 56. 133, 1887.

[2] J. Volhard (*Liebig's Ann.*, 198. 331, 1879) recommends warming the gold solution with mercuric oxide on the water bath. The particles of gold are said to aggregate with the mercuric oxide, and are, in consequence, easily filtered and washed. The mercuric oxide volatilises on ignition.

[3] The gold chloride may be partially decomposed into metallic gold, etc., during the evaporation. This does not matter.

Precipitation by Oxalic Acid—The solution is concentrated as described above, and the acid solution is neutralised and warmed with oxalic acid, until further additions of oxalic acid give no further separation of gold.[2] The reduction is best made in a covered vessel, on account of the risk of losses by the spurting which attends the oxidation of the oxalic acid to carbon dioxide. The vessel is allowed to stand in a warm place for about 24 hours, and the metallic gold is filtered, washed with water,[3] ignited in a porcelain crucible, and weighed as metallic gold.

The oxalic acid process is not satisfactory in the separation of gold from palladium, since some of the palladium is precipitated with the gold—about ½ per cent. is precipitated per gram of gold. When lead is present, it will be precipitated as oxalate with the gold. Hence, the lead must be removed or another precipitating agent substituted. If the lead be removed as sulphate, there is a danger of the latter carrying down some of the gold. If much lead and little gold be present, probably all the gold will be found with the precipitate of lead sulphate.[4] Selenium and molybdenum are not precipitated; but if insufficient hydrochloric acid be present, tellurium, if present, may give a precipitate which is removed from the gold by washing with hydrochloric acid. If much copper be present, the gold will be contaminated with copper oxalate, even if a great excess of hydrochloric acid be employed. To separate the gold from the copper oxalate, Purgotti[5] proposes the following process:—Evaporate the aqua regia solution on a water bath to dryness, dissolve the residue in water, add oxalic acid, and digest the mixture in a warm place for 48 hours. Neutralise the boiling solution with potassium hydroxide. If a great excess of oxalic acid has not been added, more will be needed so as to form a soluble double copper and potassium oxalate, which imparts an ultramarine blue tint to the solution. The precipitated gold can then be filtered from the solution and washed in the usual manner. When the above-mentioned disturbing elements are present, it is best to use the sulphurous acid or the hydrazine process.[6]

Precipitation by Hydrazine Hydrochloride.—Hydrazine hydrochloride may

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[1] It is interesting to observe in this connection that *the evaporation of alkali nitrates to dryness a number of times with hydrochloric acid is not sufficient to effect the complete conversion of the nitrates to chlorides.* For instance, 0·1893 grm. of potassium nitrate furnished after a number of evaporations:

Evaporation . . .	First.	Second.	Third. . . .	Ninth. . . .	Twelfth.	
Potassium nitrate . .	0·1136	0·0581	0·0149 . . .	0·0013 . . .	0·0013	grm.

B. Lucanus (*Zeit. anal. Chem.*, **3**. 403, 1864) prefers to ignite the alkali nitrate with four to six times its weight of grape sugar, so as to form the carbonate; and when this is treated with hydrochloric acid, the chloride will be obtained free from the nitrate.

[2] Note that most of the oxalates (excepting those of the alkalies and magnesium) are but sparingly soluble in neutral solutions and feebly acid solutions. Some dissolve in alkalies, and all dissolve in concentrated mineral acids, while some are almost insoluble in dilute acids—*e.g.*, copper oxalate in dilute nitric acid (C. Luckow, *Zeit. anal. Chem.*, **26**. 9, 1887; *Chem. News.* **55**. 73, 1887; G. Bornemann, *Chem. Ztg.*, **23**. 565, 1899; H. L. Ward, *Zeit. anorg. Chem.*, **77**. 257, 269, 1912)—hence, when other metals are present the solution should be sufficiently acid to prevent the separation of insoluble oxalates.

[3] If some of the less soluble oxalates be present, they can be removed by washing the precipitated gold with dilute hydrochloric acid.

[4] C. Whitehead, *Chem. News*, **66**. 19, 1892. [5] E. Purgotti, *Zeit. anal. Chem.*, **9**. 128, 1870.

[6] R. Fresenius (*Quantitative Chemical Analysis*, London, **1**. 477, 1876) says that the oxalic process is not satisfactory in the presence of lead, mercurous, and silver salts. Since the determinations are usually made in hydrochloric acid solutions, if the solution be dilute, practically all the silver will be precipitated as chloride. Mercurous salts cannot remain in contact with gold trichloride without reducing the latter, so that if mercury and gold are present together in solution, the mercury must be in the higher state of oxidation.

be employed to precipitate gold from neutral, acid, or alkaline solutions containing potassium, sodium, barium, strontium, calcium, magnesium, aluminium, chromium, zinc, manganese, iron, uranium, nickel, cobalt, cadmium, mercury, lead, copper, but not tin. When platinum metals are associated with the gold in a solution, the gold may be first precipitated by adding hydroxylamine hydrochloride to the solution acidified with hydrochloric acid, and digesting the mixture on a water bath for some time. The filtrate must be tested to make sure that all the gold is precipitated, because hydroxylamine hydrochloride is not so vigorous an agent as the hydrazine salt. The palladium, iridium, platinum, rhodium, and osmium remain in solution. The first four elements, if present, are precipitated by hydrazine hydrochloride in alkaline solution, but not in acid solutions.[1]

§ 222. The Separation of Gold and Platinum from Tin, Arsenic, and Antimony.

The tin group of elements cannot be quantitatively separated from the gold-platinum group by reducing agents; nor can tin be dissolved from the platinum metals by treatment with acids; and the sulphides cannot be separated by concentrated hydrochloric acid nor by sodium hydroxide. The volatilisation of tin sulphide in a stream of hydrogen sulphide is tedious and slow. The chlorides of tin, antimony, and arsenic can be volatilised in a stream of chlorine or hydrogen chloride. The volatilisation of the bromides in a stream of bromine gives better results.

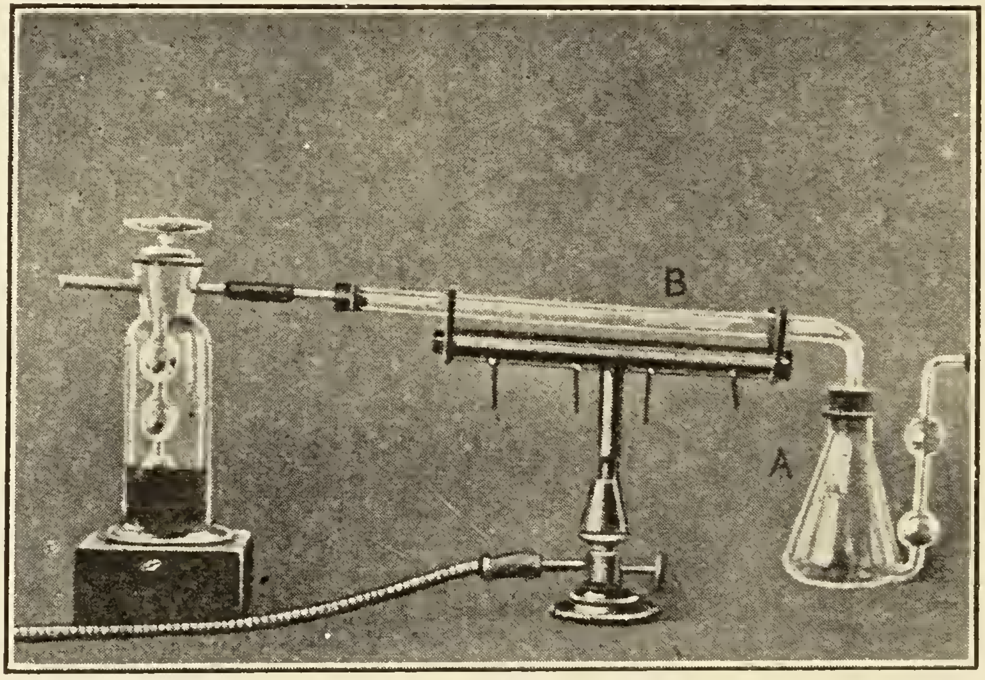

Fig. 145.—The Separation of the Tin from the Gold-Platinum group.

Volatilisation Process.—Transfer the washed sulphides to a porcelain boat along with the filter-paper ash.[2] Place the boat *B* in a hard glass combustion tube, and pass a stream of bromine or hydrogen chloride through the tube while the boat is heated as indicated in fig. 145. The exit tube leads into an absorption flask *A* containing dilute hydrochloric acid. The sulphides of arsenic, antimony, and tin are volatilised and retained by the absorption flask; any sublimate in the tube is driven away from the boat by means of the naked flame from a Bunsen's burner. The gold and platinum remain in the boat.[1] The combustion tube is washed with dilute hydrochloric acid, and the washings run into the absorption flask. The tin, arsenic, and antimony in the latter can be determined in the usual manner. The process is accurate, but it occupies a long time.

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[1] Osmium and ruthenium are only partially precipitated in alkaline solutions by the hydrazine salt, and not at all in acid solutions.

[2] The filter paper is separated from the sulphides, and burned alone. The sulphides may also be intimately mixed with 3–5 times their weight of ammonium chloride and their own weight of ammonium nitrate, and calcined. The gold and platinum remain in the crucible.

Dirvell's Process.—Dissolve the precipitated sulphides in aqua regia. Add a small quantity of a saturated neutral solution of sodium oxalate and of oxalic acid. Then add a considerable excess of sodium hydroxide—pure by alcohol. No notice need be taken of any separation of sodium oxalate. Heat the solution to boiling, and while boiling, add, drop by drop, a solution of chloral hydrate. Boil the solution under a hood.[2] When an excess of chloral hydrate has been added, and the gold and platinum have precipitated, filter the boiling solution, wash, and weigh the mixed metals in the usual manner. The filtrate is diluted with water and boiled to drive off the chloroform.[3] The antimony, arsenic, and tin are determined in the filtrate in the usual manner. The washed gold and platinum are dissolved in aqua regia and separated either by precipitating the gold with oxalic acid, or the platinum with ammonium chloride (page 436).

§ 223. The Colorimetric Determination of Gold.

Gold can be estimated, somewhat approximately, by the tint obtained when gold solution is brought in contact with a solution containing a mixture of stannous and stannic chlorides.[4] The gold sulphide is dissolved in 10 c.c. of aqua regia (three volumes of concentrated hydrochloric acid, and one volume of concentrated nitric acid), and treated with a saturated solution of stannous chloride until the yellow colour is bleached. The purple tint which develops in less than a minute is compared with a set of artificial standards made by mixing solutions of copper and cobalt salts in the required proportion. A coloration is obtained when but one part of gold per million parts of solution is present. The usual precautions for colorimetric determinations are here of exceptionally great importance in order to get reliable results. The difficulty in controlling the exact tint of the precipitated "purple of Cassius" considerably limits the scope of this process.

§ 224. The Analysis of Colours containing Purple of Cassius.

In the analysis of gold colours—which usually contain lead oxide, silver carbonate, stannic oxide, gold, boric oxide, silica, and soda—the sodium peroxide fusion (pages 226 and 475) is an excellent method of opening up the compound. One portion of the sample is fused in a porcelain crucible, and the resulting cake is employed for the determination of gold, silver, tin, and lead. The boric oxide is determined in another portion of the sample fused in a silver crucible. The alkalies are determined by the method described on page 226; the ignition is conducted in a silver crucible. The silica, alumina, etc., are determined on another portion of the sample fused in a silver crucible. The separation of the gold, silver, lead, and tin alone requires special mention.

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[1] R. Fresenius, *Zeit. anal. Chem.*, **25**. 200, 1886 ; L. Wöhler and A. Spengel, *ib.*, **50**. 165, 1911 ; L. L. de Koninck and A. Lecrenier, *Rev. Univ. Mines* (3), **2**. 98, 1888 ; L. Elsner, *Journ. prakt. Chem.* (1), **35**. 310, 1845 ; A. Béchamp and C. St Pierre, *Compt. Rend.*, **52**. 757, 1861 ; P. de Clermont, *ib.*, **88**. 972, 1879 ; G. Campari, *Ann. di Chim.*, **74**. 1, 1882 ; T. Bailey, *Journ. Chem. Soc.*, **49**. 735, 1886 ; V. Antony and L. Niccoli, *Gazz. Chim. Ital.*, **22**. ii, 408, 1892.

[2] Vapours of chloroform are evolved.

[3] P. J. Dirvell, *Bull. Soc. Chim.* (2), **46**. 806, 1886

[4] E. Sonstadt, *Chem. News*, **26**. 159, 1872 ; T. K. Rose, *ib.*, **66**. 271, 1892 ; R. N. Maxon, *Amer. J. Science* (4), **21**. 270, 1906 ; *Chem. News*, **94**. 257, 1906 ; A. Carnot, *Compt. Rend.*, **97**. 105, 1883 ; J. Moir, *Journ. Chem. Met. Soc. S. Africa*, **4**. 125, 1903 ; A. Prister, *ib.*, **4**. 235, 1903 ; H. R. Cassel, *Eng. Min. Journ.*, **76**. 661, 1903 ; E. Rupp, *Ber.*, **36**. 3961, 1903 ; M. E. Pozzi-Escot, *Ann. Chim. Anal.*, **12**. 90, 1907 ; W. Bettel, *Min. Eng. World*, **35**. 987, 1912. For the detection of traces of gold, see J. E. Saul, *Analyst*, **38**. 54, 1913.

Separation of Silver.—The fused cake is taken up with water and the solution warmed with an excess of hydrochloric acid. The gold passes into solution as gold chloride,[1] the silver is precipitated as silver chloride along with a certain amount of silica and lead. The solution is diluted, so that it contains no more than the equivalent of 0·25 to 0·30N-HCl after the alkali has been neutralised. The hot solution is filtered through a hot-jacketed funnel, and washed with $\frac{1}{4}$N-hydrochloric acid. The precipitated silver chloride is freed from silica by treatment with hydrofluoric acid, and then dissolved in ammonia.[2] The properties of silver chloride should here be studied—page 650.

Purification of Silver Chloride from Lead Chloride.—The lead chloride can be removed from the ammoniacal solution of silver chloride by adding 5 c.c. of a concentrated solution of ammonium nitrate, 40 c.c. of a 2 per cent. solution of hydrogen peroxide per 25 c.c. of the cold ammoniacal solution.[3] In 3 or 4 hours the yellowish-brown flocculent precipitate of lead peroxide may be filtered and washed, first with dilute ammonia, and lastly with cold water. The lead peroxide is dissolved in nitric acid, assisted by the addition of a little hydrogen peroxide. The lead is transformed into sulphate and weighed in the usual manner. The silver is determined by acidifying the solution with nitric acid and boiling it for a short time. The precipitated silver chloride is filtered, etc., as indicated on page 652.

Separation of Tin.—The filtrate remaining after the removal of the silver chloride contains the gold, lead, and tin. These metals are precipitated as sulphides by means of hydrogen sulphide. The sulphides are washed as indicated on page 309, and dried. The paper is ignited after the sulphides have been transferred to a porcelain boat. The ash of the filter paper is also brushed into the boat, and the tin volatilised by heating the boat, etc., in a stream of bromine (fig. 145).[4]

Separation of Gold and Lead.—The boat containing the gold and lead bromides is again introduced into a combustion tube and heated in a current of hydrogen gas with the usual precautions against explosion. Metallic gold and lead remain in the boat. The latter is alone soluble in dilute nitric acid, hence the separation is easy. Add the weight of lead sulphate finally obtained to the lead sulphate obtained from the silver, and compute the corresponding amount of lead oxide in the usual way. The gold is ignited, weighed, and reported as metallic gold.

The amount of gold in these colours is relatively small, and there is a slight loss of gold with each precipitation. The silver and gold are best determined by the fusion, cupellation, and parting processes on a separate sample, and the tin and lead by usual processes. In illustration, the analysis of a purple of Cassius colour furnished:

SiO_2.	Al_2O_3.	SnO_2.	Na_2O.	Ag.	PbO.	Au.	B_2O_3.	CO_2.	
15·10	1·21	30·19	4·49	7·00	29·23	1·44	10·50	1·20	per cent.

The carbon dioxide is determined by the method of page 553.

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[1] Although hydrogen peroxide in alkaline solution precipitates metallic gold, the hydrogen peroxide in the presence of hydrochloric acid forms chlorine, which dissolves the gold as chloride. The tin is in the form of stannic chloride, and stannic chloride gives no precipitate with gold chloride.

[2] It is sometimes difficult to dissolve all the silver chloride in ammonia. In that case, successive treatment of the precipitate on the filter paper with ammonia, boiling water, and dilute nitric acid will bring about the solution of the silver chloride.

[3] P. Jannasch, *Ber.*, **26.** 1496, 1893.

[4] If bismuth be present, it will be volatilised with the tin, and the separation of bismuth and tin can be effected by the usual methods.

Mylius' Ether Process.[1]—When acidified aqueous solutions of gold chloride in presence of many other chlorides are treated with ether, the ethereal solution which floats on the aqueous layer carries most of the gold chloride, and the chlorides of the other metals remain below in the aqueous layer. When 100 c.c. of ether were shaken with 100 c.c. of an aqueous solution containing the equivalent of 1 grm. of metal, Mylius found that the following percentage amounts passed into the ethereal solution:

	$HgCl_2$.	$AuCl_3$.	$FeCl_3$.	$SbCl_3$.	$SnCl_4$.	$AsCl_3$.
10 per cent. HCl . . .	0·4	98·2	8	22	23	7·3
1 per cent. HCl . . .	13·0	85·0	tr.	0·3	0·8	0·2

And 3·0 per cent. of $FeCl_3$; 0·05 $CuCl_2$; 0·03 $ZnCl_3$; 0·01 $NiCl_2$; 0·01 $PtCl_4$; 0·01 $PdCl_2$; 0·02 H_2IrCl_6 from the 10 per cent. acid solutions, and only traces from the 1 per cent. acid solutions. No lead or silver chloride was dissolved by the ether. Hence, by treating a solution of gold chloride containing 5–10 per cent. of gold and 5–10 per cent. of free hydrochloric and (HCl) four or five times with ether in a separating funnel, or in the apparatus, figs. 149 or 151, very good separations are said to be effected. The ether is distilled off, and the gold reduced with sulphurous acid, etc. The method promises to be useful for the separation of gold from certain metals.

§ 225. The Determination of Gold and Silver by Cupellation and Parting.

The fusion and cupellation are performed very much as indicated on page 326. but some modifications must be introduced.[2] The powdered sample should be thoroughly mixed with the flux, so that as soon as the lead is reduced it may come into contact with the gold and silver. The lead dissolves these metals, and the solution finally collects at the bottom of the crucible. The amount of reducing agent added to the fusion mixture should be proportioned to give a button weighing about 30 grms. The sample under investigation may be reducing, oxidising, or neutral, and too much or insufficient lead may be obtained.

Preliminary Assay.—It is therefore necessary to make a preliminary assay by fusing an intimate mixture of 5 grms. of the powdered sample with:

Litharge, 50 grms.; sodium bicarbonate, 18 grms.; calcined borax, 5 grms.

The mixture is placed in a crucible of such a capacity that the crucible is less than three-fourths filled, and covered with a layer of common salt.[3] The fusion is made as indicated on page 327. Break the cold crucible, if the molten mixture has not been poured into the mould. Hammer off the slag, and weigh the button. The button from 30 grms. of the sample should weigh between 16 and 20 grms. Hence, the button from the 5 grms. of the sample should weigh nearly 3 grms. Weigh the button. Suppose:

(1) The button weighs nearly 3 grms. In that case the above-mentioned mixture is the right one. Hence, fuse 30 grms. of the sample with:

Litharge, 80 grms.; sodium bicarbonate, 18 grms.; calcined borax, 5 grms.

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[1] F. Mylius, *Zeit. anorg. Chem.*, **70**. 203, 1911; F. Mylius and C. Huttner, *Ber.*, **44**. 1315, 1911.

[2] "Gold lustres," "liquid gold," etc., can be prepared for cupellation by evaporating a weighed quantity in a porcelain dish, and incinerating the carbonaceous residue to drive off the carbon. The residue may be dissolved in aqua regia and analysed by the wet process, or wrapped in sheet lead, cupelled, etc., for gold and silver.

[3] Previously fused and ground to powder.

in a suitable crucible. The mixture is covered with a layer of common salt as indicated on page 327.

(2) The button weighs over 3 grms. The sample is therefore a strong reducing agent, and this must be corrected by the addition of an oxidising agent, say, nitre. Too large a button gives low results for silver, since some silver is then lost owing to absorption by the cupel and by volatilisation, and this the more the greater the amount of lead present.

Example.—Suppose that the button weighs 7 grms. Then 30 grms. of sample would give a button weighing 42 grms., that is, 24 grms. too much lead. Since 1 grm. of nitre oxidises about 4 grms. of lead, it will be obvious that $\frac{1}{4}$ of $24 = 6$ grms. of nitre must be used with the mixture of litharge, etc., indicated in (1).

(3) If the weight of the button be less than 3 grms , the sample has but a slight reducing action, but not sufficient to give a button of normal weight. There is then a danger of some gold and silver being left in the slag. A little reducing agent—charcoal, argol, etc.—must then be added to the mixture indicated in (1).

Example.—Suppose the button weighed 2 grms., the button from 30 grms. of the sample would weigh $2 \times 6 = 12$ grms. Hence, in order to get a button weighing 18 grms., enough reducing agent to give 6 more grms. of lead is needed. One grm. of argol is found to reduce 10 grms. of lead from litharge. Hence, it is necessary to add $\frac{1}{10}$ of $6 = 0{\cdot}6$ grm. of argol to the mixture indicated in (1).

(4) If no button is obtained, the sample is either neutral or oxidising. In the former case, the fusion can be made with 2 grms. of argol, 30 grms. of the sample, and the normal fusion mixture. If the sample be oxidising, the button may still be too small. In that case, the weight of the button obtained will furnish data for calculating how much more argol will be required to give a button of normal weight.

Example of Assay.—The preliminary fusion of a sample of gold colour showed no button of lead, and the fusion of 30 grms. of the sample with 50 grms. of litharge, 1·5 grms. of argol, 18 grms. of sodium bicarbonate, and 5 grms. of calcined borax, gave a button weighing just less than 20 grms.

If the charge in the crucible contains much nitre, and uncalcined borax, it is liable to froth over. To prevent this, start the fusion at a low temperature and raise the temperature very slowly. If the bubbling be still troublesome, it may be advisable to roast the sample in a shallow clay "roasting dish" in the muffle, and take portions of the roasted sample for the preliminary and final assay. The final results must of course be expressed in terms of the roasted sample.

We may now assume that the fusion and the cupellation have been performed as indicated on page 326. The bead of silver and gold is weighed. The separate determination of the gold and silver involves the two operations of inquartation and parting.[1]

Inquartation and Parting.—The latter term is applied to the process of separating gold and silver by the action of acid on the bead or "prill" obtained during cupellation. Nitric or sulphuric acids may be used, but the former is almost universally employed. Silver is soluble in nitric acid, gold is not. If an alloy of silver and gold be digested with nitric acid, silver, not gold, is dissolved. It is necessary that at least twice as much silver as gold be present to ensure the dissolution of all the silver by nitric acid of specific gravity not less than 1·26, and boiling for half an hour. But, as a matter of fact, in parting all bullion assays, five times as much silver as gold is considered necessary. For successful parting, therefore, special attention must be paid to:

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[1] The "gold" obtained by burning "gold rags" from the "decorating shop" of a pottery is evaluated in this way.

(1) The concentration of the nitric acid. For general work, an acid of the strength recommended by Keller[1] may be used, namely, 1 part of concentrated nitric acid (sp. gr. 1·42) with 9 parts of distilled water. With this acid, Keller says the gold remains as a coherent mass, even if 500 times as much silver as gold be present. The beads are supposed to be boiled in the acid about 15 minutes. There are, however, certain advantages in employing acids of two different strengths, as indicated below.

(2) The temperature of the acid. The acid should be boiling when the bead to be parted is dropped into the flask. If the bead be dropped into cold acid, and then heated up to the boiling point, the gold is liable to disintegrate into a finely divided condition—especially if the proportion of silver is large,—and this may lead to loss in subsequent operations.

(3) The ratio of silver to gold in the bead. Although the ratio 5 : 1 is usually recommended, this is not quite under control. If less than this amount of silver be present, more silver can be added to the crucible when the fusion is made for the cupellation; or to the lead button during cupellation when gold alone, and not silver, is to be determined. If silver and gold are to be determined, the bead, after cupellation, is weighed. This weight represents silver + gold. A small piece of pure sheet lead weighing about 2 grms. is folded in the shape of a hollow cone. The necessary amount of pure silver is placed in the cone, which is then closed and folded into a little packet. This is then cupelled. Instead of this recupellation, some prefer to alloy the silver with the bead by fusion on charcoal before the blowpipe. The latter operation requires some practice for successful work. The process of alloying silver with the cupelled bead in order to prepare it for parting is called "inquartation," because formerly at least three parts of silver to one of gold were considered necessary for successful parting.

With practice, the amount of silver needed can be estimated from the colour of the bead. If the bead is white, it contains more than three parts of silver to one of gold, and inquartation may be unnecessary, or the bead may be inquarted with its own weight of silver. If the bead is greenish yellow, it probably contains less than three parts of silver to one of gold, and the bead is inquarted with about twice its weight of silver. If the bead is yellow or reddish yellow, the gold predominates, and it is inquarted with two or three times its weight of silver. A set of standard prills can be easily made for comparison.

The "quarted" alloy is removed from the cup with the "bead forceps," cleaned with the "button brush," and hammered on an anvil to a flat disc about 1 mm. thick. The metal becomes hard and brittle during the hammering, and the disc is accordingly annealed by heating it to dull redness while supported on a clean cupel, and cooling it rapidly on a piece of brass foil. The bead is then rolled between two steel rollers so as to form a long strip. If the disc had been rolled without annealing, the edges of the strip would probably be rough, and little pieces would drop off during the action of the acid. The strip is again annealed and rolled. The roll is placed in a small parting flask[2] containing about 30 c.c. of nitric acid[3] (sp. gr. 1·2), previously heated to about 90°. The acid is boiled[4] for about 20 minutes; cooled; and decanted off. The roll is washed twice with distilled water. 30 c.c. of boiling concentrated nitric acid

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[1] E. Keller, *Trans. Amer. Inst. Min. Eng.*, **36**. 3, 1905

[2] There are several different forms. The flasks are better without a lip. Some prefer to conduct the parting in small glazed porcelain crucibles. The "cupping" described in the text is then unnecessary.

[3] Free from chlorine, sulphuric and sulphurous acids, and sulphides.

[4] If the bead turns black and the action stops, insufficient silver is probably present. The bead is then flattened and fused with two or three times its weight of silver and re-parted.

(sp. gr. 1·3) are then added to the flask containing the roll. After 20 minutes' boiling,[1] decant off the acid, and wash three times by decantation with distilled water.[2] Fill the flask to the very top with distilled water, and place a close-fitting porcelain capsule—"parting cup"—over the mouth of the flask. Invert the flask (fig. 146). The roll settles in the parting cup. The flask is removed by raising its mouth to the level of the water in the crucible, and moving the flask at right angles away from the parting cup to allow the water to run away. The water is decanted from the parting cup. The cup and contents are dried by holding the cup with a pair of tongs in the flame of a Bunsen's burner until the cup is red-hot.[3] The gold is annealed, and changes from a soft dark brown condition to hard yellow gold.[4] When cold, weigh. Subtract the weight of the gold so obtained from the weight of the original prill to get the approximate weight of silver in the given sample.

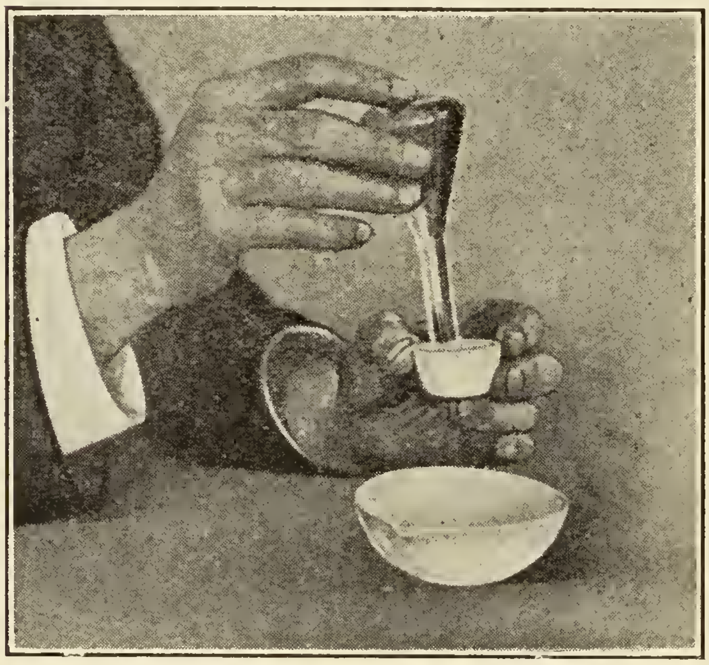

FIG. 146.—"Cupping."

Errors.—The errors in the cupellation process involve:—

(1) The retention of gold by the slag during fusion.—If the amount of collecting lead is ample, the error is not serious.[5] Buttons less than about 20 grms. should not be used. The loss is largely dependent on the nature of the impurities which pass into the slag.

(2) The loss of gold by volatilisation.—Gold begins to volatilise about 1070°, and silver at about 680°; hence gold and silver may be volatilised during fusion and cupellation. The loss is greater the higher the temperature of cupellation.[6]

(3) The absorption of gold by the cupel.—The amount varies with the nature of the bone ash used in making the cupel. The loss of gold is greater the higher the temperature of cupellation.[7]

(4) The retention of lead by the cupelled beads.—A little lead is almost invariably retained by the bead cupelled at the regular temperatures. Hillebrand and Allen[8] found about 0·3 per cent. loss with a 0·09 grm. bead of gold.

(5) The solution of gold by the parting acid.—During parting a trace of gold

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[1] By first boiling with a dilute acid, and afterwards with a more concentrated acid, the removal of the silver is more complete, the gold becomes more compact, and there is less risk of disintegrating the residual gold.

[2] If the gold disintegrates, there will probably be losses in transferring.

[3] The drying must be carefully done, or particles of gold may be spurted from the cup with the steam. The drying, etc., may be done by placing the cup in the red-hot muffle for a short time.

[4] If the dish shows a black stain after it has been heated, the washing was imperfectly done, and the analysis or assay should be repeated. If, after parting, the amount of gold is more than one-third the weight of the bead, it must be fused with about three times its weight of silver and again parted.

[5] E. H. Miller and C. H. Fulton, *School Mines Quart.*, **17**. 160, 1896; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**. 24, 1905.

[6] G. H. Makins, *Journ. Chem. Soc.*, **13**. 77, 1860; T. K. Rose, *ib.*, **63**. 707, 1893; J. Napier, *ib.*, **10**. 229, 1858; W. Witter, *Chem. Ztg.*, **23**. 522, 1889; H. Rössler, *Dingler's Journ.*, **206**. 189, 1884; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**. 19, 1905; K. Friedrich, *Zeit. angew. Chem.*, **16**. 269, 1903; J. W. Richards, *Chem. News*, **74**. 2, 1896.

[7] A. F. Crosse, *Journ. Chem. Met. Soc. S.A.*, **2**. 325, 1902; T. L. Carter, *Eng. Min. Journ.*, **78**. 728, 1902; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **253**. 19, 1905.

[8] W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**. 23, 1905.

appears to be dissolved by nitric acid, even if it be free from the deleterious impurities hydrochloric acid or chlorine. This amounts to about 0·01 to 0·03 per cent. on a half-gram bead.[1]

(6) The retention of silver by the parted gold.—The amount of silver which resists attack by the acid varies with the percentage of silver alloyed with the gold to be parted.[2] It amounts to from 0·05 to 0·10 per cent. under ordinary conditions, and it is generally considered to be least when the alloy contains between 1·0 and 2·5 per cent. of silver. If more or less silver be present, the gold will be contaminated with more silver after parting. Other foreign elements—copper, tellurium, etc.—may be retained by the bead.

(7) The occlusion of gases by the gold.—According to Graham,[3] about two parts by weight per 10,000 parts of gold are retained by the annealed gold. The amount depends upon the temperature of annealing.

Some of these errors obviously lead to low results, others to high results. Experience shows that under normal conditions both sets of errors are small, and tend to neutralise one another. The algebraic sum of the losses and gains is called the *surcharge*, and the surcharge can be approximately determined by control experiments with the purest available gold and silver. Since the purity, *i.e.* the fineness, of gold is usually reported in parts per 1000, a surcharge of $+0·2$ means that the gold actually reported weighed 0·2 part per 1000 more than was present; and conversely with a surcharge of $-0·2$.

It must be added that the greatest care must be exercised in weighing the gold. A balance even more sensitive than $\frac{1}{200}$ mgrm. is a distinct advantage. The precautions indicated in the first chapter require serious attention. Under favourable conditions, and weighing correctly to 0·01 per 1000, Rose[4] considers that the operations can be conducted with an error not exceeding $\pm 0·02$ part per 1000.

§ 226. The Determination of Platinum and the "Platinum Metals."

The Cupellation Process for Gold, Silver, and Platinum.—When gold is determined by the process described in the preceding section, the bead will have a greyish colour if small amounts of platinum be present;[5] and if larger amounts be present, the bead will have a rough "frosted" appearance, because it "freezes" before all the lead is oxidised. The method used for separating platinum, under these conditions, depends on the solubility of platinum in nitric acid when the metal is alloyed with at least 12 times its weight of silver.[6] Platinum can be separated from gold by cupelling the cornet with about 12 times its weight of silver, and parting with hot nitric acid (sp. gr. 1·42).[7] The residual gold is washed, dried, and weighed.[1] The operations are repeated until the residual gold has a constant weight, showing that all the platinum has been removed.[2]

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[1] A. H. Allen, *Chem. News*, **25**. 85, 1872; V. Lenher, *Journ. Amer. Chem. Soc.*, **26**. 552, 1904.

[2] W. F. Lowe, *Journ. Soc. Chem. Ind.*, **8**. 687, 1889; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **523**. 25, 1905; T. K. Rose, *The Metallurgy of Gold*, London, 485, 1906.

[3] T. Graham, *Phil. Trans.*, **156**. 433, 1866.

[4] T. K. Rose, *Journ. Chem. Soc.*, **63**. 700, 1893.

[5] In cupelling alloys of platinum, gold, silver, and lead, the greater the proportion of platinum the higher the temperature required for the cupellation. Alloys with over 50 per cent. of platinum cannot be freed from lead except at the temperature of the oxyhydrogen flame.

[6] C. Winkler, *Zeit. anal. Chem.*, **13**. 369, 1874: P. Oehmichen, *Berg. Hütt. Ztg.*, **60**. 137, 1901; M. Trenkner, *Met.*, **9**. 103, 1912; *Min. Eng. World*, **37**. 342, 1912.

[7] J. Spiller (*Proc. Chem. Soc.*, **18**. 118, 1897) states that nitric acid (sp. gr. 1·42) will dissolve 0·75 to 1·25 per cent. of platinum along with silver; while a weaker acid (sp. gr. 1·2) will dissolve only 0·25 per cent. of platinum; and a stronger acid will lead to the separation of platinum black. E. Přiwoznik, *Berg. Hütt. Ztg.*, **44**. 325, 1895; H. Carmichael, *Journ. Soc. Chem. Ind.*, **22**. 1324, 1903.

The silver solution is largely diluted with water, or, better, evaporated to drive off the excess of acid and then treated with a dilute solution of hydrogen sulphide. The silver sulphide which separates carries down the platinum as well.[3] Let the mixture stand overnight. Filter and wash in a porcelain dish. Dry the precipitate and ignite it with the filter paper at a low temperature. Wrap the residue in a small piece of "assay lead-foil," and cupel. The resulting bead is parted with concentrated sulphuric acid, when the platinum remains behind as a dark spongy mass. The sponge is again boiled with fresh acid, washed by decantation, dried, and weighed as platinum.[4]

The first cupellation enables the gold, silver, and platinum to be estimated; the result of the nitric acid parting gives the gold; and the sulphuric acid parting, the platinum; the silver is obtained by difference.

The Separation of Platinum by Potassium or Ammonium Chloride.—Platinum[5] can be separated from solutions containing the copper and aluminium groups[6] by almost neutralising the acid solution with ammonia, evaporating the solution to the crystallisation point, and adding water in sufficient quantity to just dissolve the crystals. Then add an excess of a saturated solution of potassium chloride to the feebly acid solution, and, after well mixing, add an excess of alcohol. Cover the vessel with a clock-glass, and let the mixture stand in a warm place for about 24 hours. Collect the precipitate on an asbestos-packed Gooch's crucible, and wash the precipitated K_2PtCl_6 with 80 per cent. alcohol, as indicated for the determination of potassium (page 234). The potassium chloroplatinate can be dried and weighed; or reduced to metal and the metal weighed. Ammonium chloride is preferable to potassium chloride as precipitant, because the resulting ammonium chloroplatinate, $(NH_4)_2PtCl_6$, can be washed with a saturated solution of ammonium chloride, and ignited—very gently at first to avoid the risk of loss by spurting. The metallic platinum which remains behind can be weighed directly. If iridium be present in the solution, it would also be precipitated with the ammonium chloroplatinate, to which it imparts a reddish tinge. If the ignited mass be digested with dilute aqua regia (1 : 5)[7] at 40°, the platinum dissolves and metallic iridium remains as an insoluble black powder. This is washed, dried, and weighed.

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[1] If the gold be very finely divided, it is best to filter and wash, so that the fine particles of gold will not contaminate the silver solution.

[2] If palladium be present, it will dissolve with the silver; while if iridium be present, it will remain with the gold. E. H. Miller, *School Mines Quart.*, **17**. 26, 1896.

[3] F. P. Dewey, *Journ. Ind. Eng. Chem.*, **4**. 257, 1912; *Min. Eng. World*, **36**. 503, 1912. Traces of gold in solution of silver could also be gathered with the silver in a similar way.

[4] To make sure the residue is platinum, dissolve it in a few drops of aqua regia, evaporate the solution to drive off the excess of acid, and test it qualitatively with potassium iodide, or ammonium chloride. If palladium was present in the original sample it will be found in the acid solution after parting. According to A. C. Dart (*Met. Chem. Eng.*, **9**. 75, 1911; **10**. 219, 1912), the silver can be precipitated as chloride; and the palladium precipitated as metal, by boiling the filtrate, made ammoniacal with ammonia and acidified with formic acid. The silver chloride, it may be added, is very liable to carry down traces of other metals. If iridium be associated with the gold, the latter can be removed by digesting the mixture at 40°, with a mixture of nitric acid (sp. gr. 1·34) with three times its volume of hydrochloric acid, and all diluted with five times its volume of water. The washed and dried residue is iridium. The difference in the two weighings represents the gold.

[5] The general properties of platinum were discussed in dealing with gold.

[6] Metals precipitated by soluble chlorides—silver, lead, and mercurous salts—are supposed to be absent.

[7] Iridium is soluble when heated with concentrated aqua regia. "Iridium grey" and "platinum grey" colours can be analysed by these processes.

General Analysis of the Platinum Metals.[1]—It is not often that an analysis of this kind is needed.[2] The sample is treated with concentrated aqua regia at 70°, and evaporated to a small volume.[3] More hydrochloric acid is added, and the solution evaporated to dryness. The mass is digested with warm water, and the insoluble residue—probably osmiridium—filtered off. Fuse one part by weight of sodium hydroxide in a copious nickel crucible, and add gradually an intimate mixture of one part of the insoluble residue with four parts of sodium peroxide. Keep the mass in a semi-fluid condition for about half an hour, and stir frequently with a nickel spatula. Dissolve the cold mass in dilute hydrochloric acid, and add the liquid to the main solution. The acid solution may contain salts of gold, osmium, rhodium, platinum, palladium, ruthenium, iridium, along with chromium, manganese, iron, etc., and of nickel from the crucible.[4]

1. *Removal of Osmium and Ruthenium.*[5]—If the solution contains osmium and ruthenium, these elements are best removed at this stage by connecting a distilling flask (fig. 147) by means of ground glass joints with a pair of Wölbling's absorption flasks[6] containing dilute hydrochloric acid (1 : 2). The Wölbling's flasks are placed in a dish con-

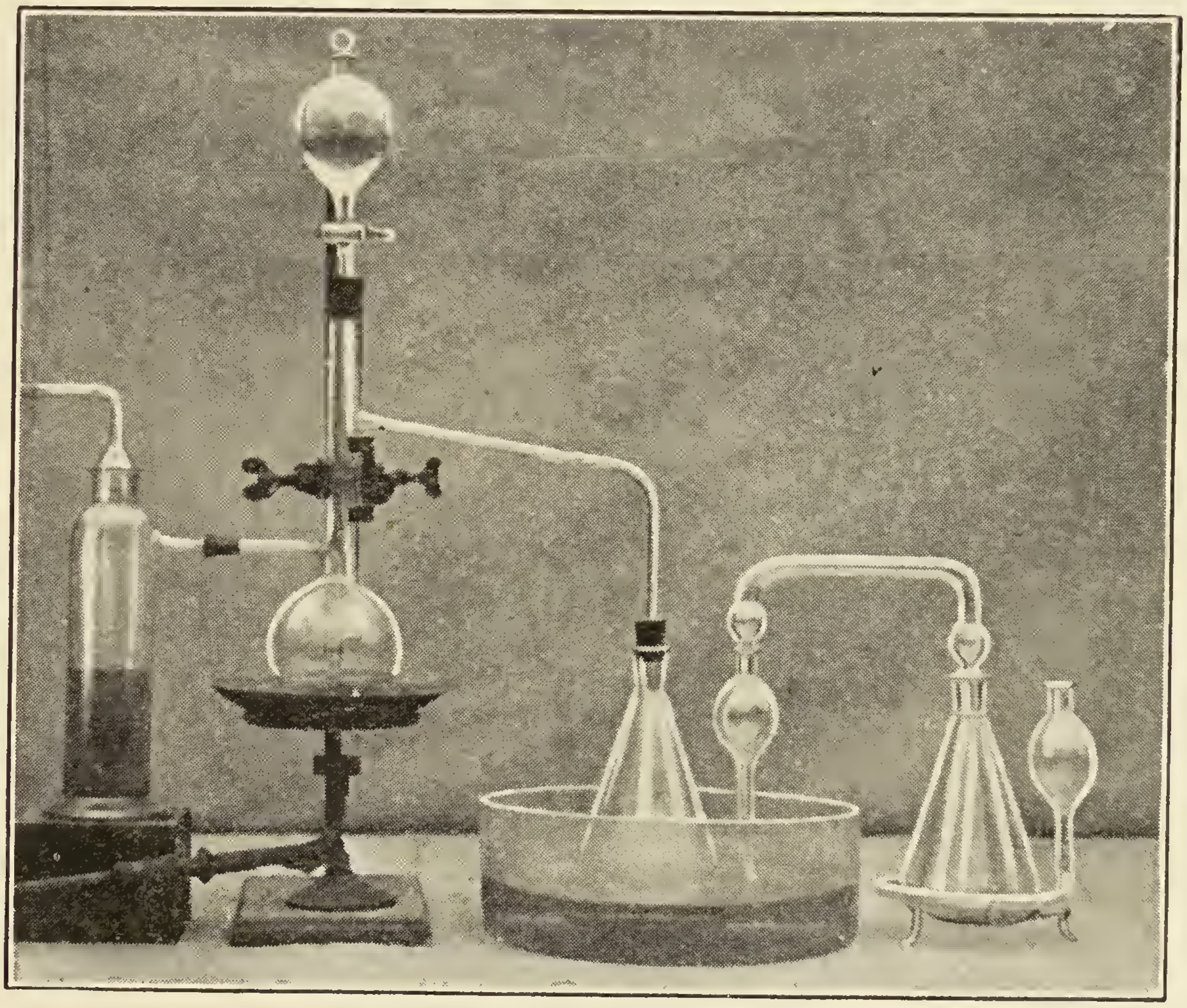

Fig. 147.—Separation of osmium and ruthenium from the other "platinum metals."

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[1] L. E. Rivot, *Docimasie*, Paris, **4**. 1103, 1866 ; R. Jagnaux, *Analyse Chimique des Substances, Commerciales, Minérales et Organiques*, Liège, 1888 ; W. Crookes, *Select Methods in Chemical Analysis*, London, 437–477, 1905 ; H. St C. Deville and H. Debray, *Ann. Chim. Phys.* (5), **56**. 439, 1859 ; R. W. Bunsen, *Liebig's Ann.*, **146**. 265, 1868 ; C. Claus, *Beiträge zur Chemie der Platinmetalle*, Dorpat, 1854 ; M. C. Lea, *Chem. News*, **10**. 279, 301, 1864 ; **11**. 3, 13, 1865 ; *Amer. J. Science* (2), **38**. 81, 248, 1864 ; W. Gibbs, *ib.* (2), **31**. 63, 1861 ; (2), **34**. 353, 1862 ; E. Leidié, *Compt. Rend.*, **131**. 888, 1901 ; *Bull. Soc. Chim.* (3), **27**. 179, 1901 ; F. Mylius and F. Förster, *Ber.*, **25**. 665, 1892 ; H. Arnold, *Zeit. anal. Chem.*, **51**. 550, 1912 ; E. V. Koukline, *Rev. Met.*, **9**. 815, 1912 ; T. Wilm, *Ber.*, **18**. 2536, 1885.

[2] Some difficulties in the manufacture of "platinum lustres" have been attributed to the presence of elements of this group other than platinum.

[3] If osmium and ruthenium be present in the soluble portion, which is not likely, the operation must be conducted in a flask fitted with condensing tubes as illustrated in fig. 151.

[4] E. Leidié and M. Quennssen, *Bull. Soc. Chim.* (2), **25**. 840, 1901 ; (2), **27**. 179, 1902.

[5] A. Joly, *Encyc. Chim. de Fremy*, Paris, **3**. 236, 1892.

[6] H. Wölbling, *Chem. Ztg.*, **33**. 499, 1909.

taining ice-cold water. The liquid under investigation is poured into the distilling flask with an excess of sodium hydroxide, and a slow current of chlorine[1] is bubbled through the liquid. When the liquid in the flask is saturated with chlorine, raise its temperature to about 70°. The osmium and ruthenium form tetroxides—RuO_4 and OsO_4—which collect in the condensing flasks. The liquid in the distilling flask must be kept alkaline[2] to prevent the action of hydrochloric acid on the iridium tetroxide, and the subsequent volatilisation of iridium chloride. When all the ruthenium has volatilised,[3] the current of chlorine is stopped, and the apparatus cooled. The ruthenium tetroxide in the condensing flask forms a stable trichloride, $RuCl_3$, while the osmium tetroxide undergoes no change.

2. *The Separation of Ruthenium and Osmium.*—The liquid from the condensing flasks is treated with hydrogen sulphide so as to precipitate both sulphides. Wash and dry the precipitate, and heat it in a weighed platinum boat in a current of oxygen—fig. 122. The ruthenium remains behind as oxide, while the osmium and sulphur pass on to the condensing flasks containing a 12 per cent. solution of sodium hydroxide mixed with 2 per cent. of alcohol. The solution of sodium osmiate in the condensing flasks has probably a violet colour. If not, warm the flask gently until a violet coloration does appear—if osmium is present. Add strips of aluminium in small quantities at a time. The aluminium dissolves in the sodium hydroxide and reduces the osmium to metal. When the solution is decolorised, and all the aluminium has dissolved, wash the osmium by decantation first with water, and then with 5 per cent. sulphuric acid. Collect the precipitate in a weighed, stoppered filter tube (fig. 204) packed with asbestos. Wash with 5 per cent. sulphuric acid, and then with water. Dry at a dull red heat in a current of hydrogen, and when cold displace the hydrogen with carbon dioxide, and weigh. To check the result, expel the osmium from the tube by heating it at a red heat in a current of oxygen, and weigh again.

3. *The Separation of Iridium.*—Boil the solution to expel free chlorine, and ignore the separation of a precipitate from the faintly acid solution. Add ammonium chloride to the solution, and then two-thirds its volume of alcohol. Let the mixture stand about 24 hours. The precipitate contains most of the platinum and iridium, and traces of palladium and rhodium. Filter and wash the precipitate with dilute alcohol. The filtrate is evaporated almost to the point of crystallisation, and if a solid separates, filter and wash it with a solution of ammonium chloride. Call the filtrate A. Calcine the two mixed precipitates in a Rose's crucible (fig. 138) in an atmosphere of hydrogen. The reduced metals are digested with dilute aqua regia (1 : 5). The platinum and palladium pass into solution, the iridium and rhodium remain undissolved. Filter and wash. Call the filtrate B. The insoluble residue is carefully fused with potassium bisulphate so as to avoid loss by spurting (page 185). A rhodium salt is formed which passes into solution ; the iridium is oxidised, but it does not dissolve. The cold cake is digested in water acidified with sulphuric acid, and the insoluble mass is reduced by calcination in an atmosphere of hydrogen, washed, dried, and weighed as *iridium.*[4] The filtrate—tinged red, pink, or yellow—is boiled with an excess of sodium carbonate ; acidified with hydrochloric acid ; and the precipitate is calcined, and set aside, labelled No. I.

4. *The Separation of Platinum.*—The dilute aqua regia solution, filtrate B, contains platinum and a trace of palladium ; it is evaporated to dryness with sodium carbonate ; calcined in a Rose's crucible in an atmosphere of hydrogen ; washed with boiling water ; and the insoluble mass weighed as platinum.[5] The filtrate and washings are rejected.

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[1] Say, from a chlorine bomb and a wash-bottle (fig. 147).

[2] If necessary, add more sodium hydroxide *viâ* the stoppered funnel.

[3] A drop of the distillate will give no blackening with hydrogen sulphide if the action is over.

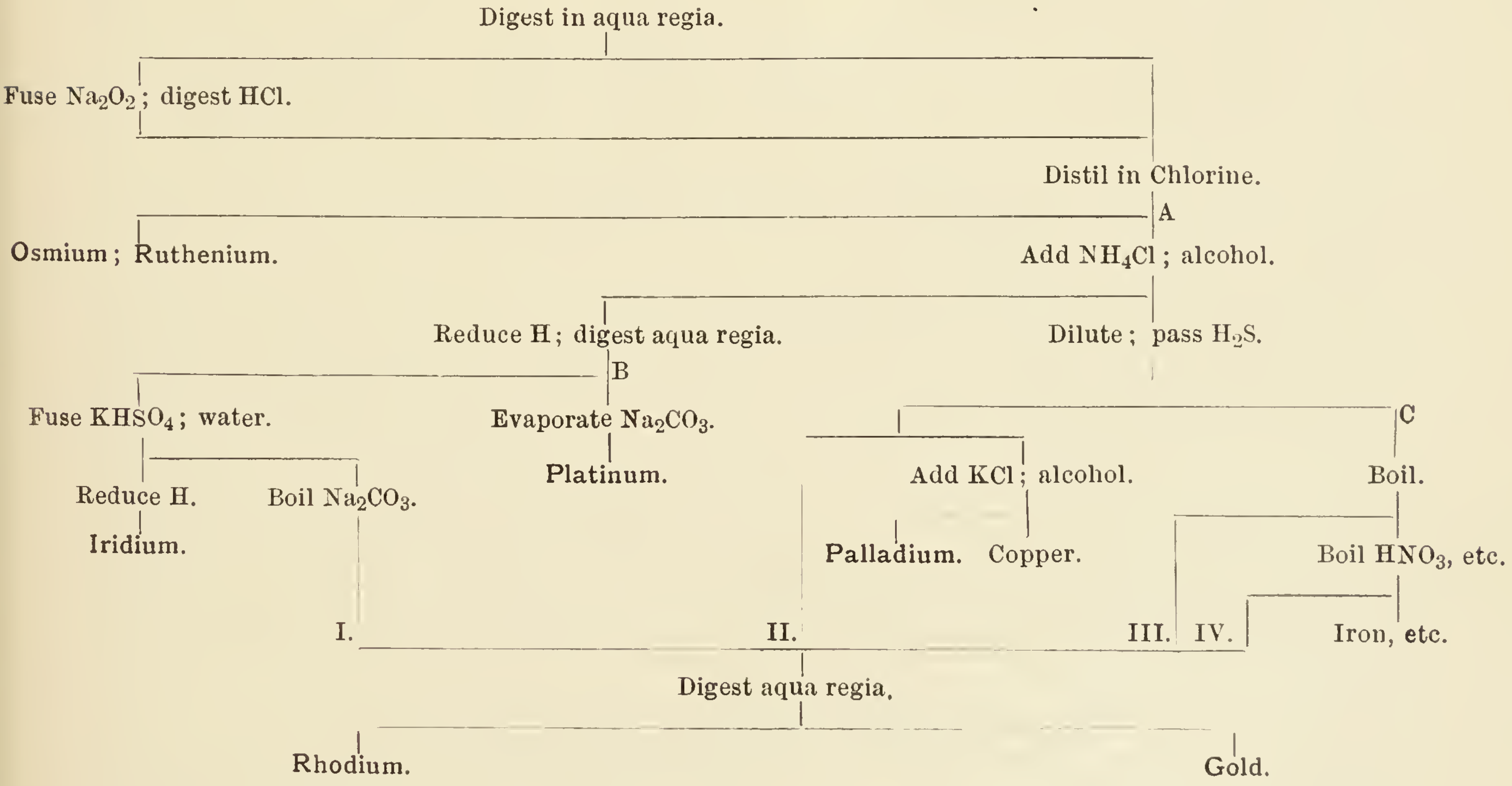
[4] This may contain a trace of rhodium. For a further purification, see Claus (*l.c.*), and Deville and Debray (*l.c.*).

[5] The precipitate may contain traces of iridium and palladium. For a further purification, see Deville and Debray (*l.c.*).

5. *The Separation of Palladium.*—The alcoholic filtrate A is diluted with water, and the acid nearly but not quite neutralised with ammonia. The liquid is saturated with hydrogen sulphide. Filter and wash. Call the filtrate C. The precipitate, containing insoluble sulphides of gold, copper, palladium, and rhodium, is roasted and then digested in hydrochloric acid. The insoluble mass is labelled No. II.; it contains gold and rhodium; the filtrate containing palladium and copper is treated with potassium chloride and alcohol to precipitate brownish-red potassium chloropalladite, K_2PdCl_4. This is decomposed by ignition; washed; dried; and the *palladium* weighed as metal. The filtrate containing copper is treated in the usual manner (page 350).

6. *The Separation of Rhodium and Gold.*—The filtrate C from the precipitated sulphides of gold, etc., contains possibly a trace of gold and of rhodium together with metals of the iron-aluminium group. When this liquid is boiled, the gold, rhodium, and some sulphur are precipitated. The precipitate is washed, calcined, and digested with hydrochloric acid, and labelled No. III. The filtrate is treated with nitric acid and evaporated to dryness; the residue is calcined; washed with hydrochloric acid; dried; and labelled No. IV. The washings contain the iron, nickel (from the crucible), etc. These elements are separated as usual. The four residues, labelled Nos. I. to IV., are mixed together and digested with aqua regia. The gold dissolves, and the rhodium remains insoluble. Filter and wash. Precipitate the *gold* from the filtrate in the usual manner; wash, dry, and weigh the insoluble powder as metallic *rhodium*.[1]

The above method gives a very fair approximation. The results check very fairly against more elaborate schemes. The operations may now be summarised:



§ 227. The Detection of Selenium.

Selenium and tellurium determinations[2] are very rarely needed in technical analyses for the silicate industries. Selenium is used in the preparation of certain reddish colours, and in bleaching and decolorising glasses and special enamel frits.[1] In the latter case, the amount in question may vary from 0·002 to 0·004 per cent., and a qualitative test may then reveal whether or not selenium is present; but quantitative determinations are only satisfactory if a relatively large amount of the material is taken for the analysis.

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[1] It will be observed that traces of the platinum metals which escape precipitation accumulate with the gold and rhodium.

[2] Tellurium determinations are chiefly required in the analysis of cupriferous pyrites and auriferous ores for metallurgical purposes.

In the regular course of qualitative analysis, selenium (and tellurium) appear as members of the sub-group of elements whose sulphides are precipitated by hydrogen sulphide in acid solutions, and whose sulphides are also soluble in sodium monosulphide. If the selenium sulphide be precipitated from a cold solution, the lemon-yellow selenium sulphide—SeS_2—is readily dissolved by alkaline sulphides. If the solution be hot, the precipitate is orange-yellow, and is much less soluble. Hydrogen sulphide separates selenium from the elements which do not give precipitates with hydrogen sulphide in acid solutions, but *selenium sulphide*[2] *cannot be quantitatively separated from the mixed sulphides of the hydrogen sulphide group by the action of sodium or ammonium sulphides.* Part of the selenium passes into solution, and part remains associated with the insoluble sulphides. In fact, from two-thirds to seven-eighths of the total selenium may remain with the insoluble sulphides of copper, bismuth, and lead. For example, a solution of copper and selenium in dilute hydrochloric acid, just acid enough to prevent the precipitation of copper selenite, was treated[3] with hydrogen sulphide. The precipitate was digested with concentrated sodium monosulphide, washed with water containing a little sodium sulphide, the water containing a little hydrogen sulphide, and finally with strong alcohol. The insoluble part, in four experiments, contained:

Sulphur	0·3787	0·1649	0·1730	0·0416	grm.
Selenium	0·2828	0·1726	0·1565	0·0239	grm.
Copper	0·9880	0·4880	0·4909	0·0979	grm.

Hence, the alkali sulphide effects a very imperfect separation when selenium and copper are together precipitated in an acid solution. The process, however, is used in qualitative analysis.

Selenium is precipitated from the ammonium or sodium sulphide solution by treatment with acids.[4] The washed and dried precipitate is mixed with twice its weight of a flux made by mixing equal parts of sodium nitrite and sodium carbonate. The mixture is added to the crucible containing two parts by weight of previously fused sodium nitrite. The fluid mass is poured on to a porcelain slab, and the cold masses (in the crucible and on the slab) are extracted with water—sodium antimoniate, stannic oxide (gold, platinum, and iridium) remain insoluble; selenic (telluric), molybdic, and arsenic acids are dissolved. Add an excess of hydrochloric acid, and boil the solution to reduce the sodium selenate, Na_2SeO_4, to selenious acid, H_2SeO_3:

$$Na_2SeO_4 + 4HCl = 2NaCl + H_2SeO_3 + H_2O + Cl_2.$$

Then boil the solution with ammonium sulphite, sulphurous acid, hydrazine sulphate, hydroxylamine,[1] or some other suitable reducing agent.[2] Brown or red-coloured selenium is precipitated.[3]

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[1] F. Kraze, *Sprechsaal*, **45**. 214, 227, 1912; P. Fenaroli, *Chem. Ztg.*, **36**. 1149, 1912.

[2] According to B. Rathke (*Liebig's Ann.*, **152**. 181, 1869; *Ber.*, **18**. 1534, 1885; **36**. 594, 1903), the precipitate is a mixture of SeS_2, Se_2S, and S. Some hold that the precipitate from selenious acid is a mixture of selenium and sulphur. H. Rose, *Pogg. Ann.*, **107**. 186, 1859; **113**. 473, 1861; E. Divers and M. Shimose, *Chem. News*, **51**. 199, 1885.

[3] E. Keller, *Journ. Amer. Chem. Soc.*, **19**. 771, 778, 1897.

[4] The ammonium or sodium sulphide solution contains selenium, molybdenum, tin, antimony, arsenic, tellurium, gold, platinum, etc.

For opening glasses and frits, treat 5 grms. of the finely powdered material with sulphuric and hydrofluoric acid in the usual manner. Evaporate the solution to dryness. Digest the residue with water, and filter. Selenium can be precipitated from the residue by boiling with a reducing agent. The aqueous extract of the sodium carbonate fusion can also be acidified and treated in a similar manner.

§ 228. The Gravimetric Determination of Selenium—Sulphurous Acid Process.

Mix the powdered substance with 6 parts by weight of sodium carbonate and 1 part of sodium nitrite in a nickel crucible.[4] Raise the temperature very gradually until the mass is fused. Extract the cold mass with water. Sodium selenate passes into solution.[5] Acidify the solution with hydrochloric acid, and boil it until chlorine[6] is no longer evolved—starch paper held in the steam will show this.[7] The boiling solution is saturated with sulphur dioxide.[8] Selenium is precipitated. The boiling is continued for about 15 minutes.[9] The precipitate becomes more compact and easier to filter after boiling. The colour also changes from red to dark brown. Test the filtrate, or a little of the clear liquid, with more reducing agent—say ammonium bisulphite—to make sure that precipitation is complete. If not, add more reducing agent and repeat the sequence of operations.[1] Collect the red precipitate on a Gooch's crucible; wash with hot water, then with alcohol, and finally with ether. Dry the crucible between 100° and 105°, and weigh as selenium—Se.[2]

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[1] P. Jannasch and M. Müller, *Ber.*, **31.** 2388, 2393, 1898; A. Gutbier, *Ber.*, **34.** 2724, 1901; R. Rosenheim and M. Weinheber, *Zeit. anorg. Chem.*, **69.** 266, 1911. For tellurium it is recommended that the reduction be effected in a weakly alkaline solution with a 10 per cent. solution of hydrazine sulphate contained in a beaker placed in an autoclave heated to 130° under a pressure of 3 or 4 atmospheres.

[2] Phosphorous acid (H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2.** 441, 1871; A. Gutbier, *Zeit. anorg. Chem.*, **41.** 448, 1904); potassium iodide and hydrochloric acid (A. W. Peirce, *Amer. J. Science* (4), **1.** 416, 1896; *Zeit. anorg. Chem.*, **12.** 409, 1896; F. A. Gooch and W. G. Reynolds, *ib.* (3), **50.** 254, 1895; W. Mathmann and J. Schäfer, *Ber.*, **26.** 1008, 1893); glucose (F. Stolba, *Zeit. anal. Chem.*, **11.** 437, 1872); magnesium or aluminium (L. Kastner, *ib.*, **14.** 142, 1875); hypophosphorous acid (A. Gutbier and E. Rohn, *Zeit. anorg. Chem.*, **34.** 448, 1903; A. Gutbier, *ib.*, **32.** 295, 1902); stannous chloride (A. Grak and J. Petrén, *Svensk. Kem. Tidschrift*, **24.** 128, 1912). For a general criticism of reducing agents, see A. Gutbier, G. Metzner, and J. Lohmann, *Zeit. anorg. Chem.*. **41.** 291, 1904. Hydrazine salts and sulphurous acid are recommended.

[3] H. Rose (*Zeit. anal. Chem.*, **1.** 73, 1862; *Pogg. Ann.*, **113.** 472, 624, 1861; *Chem. News*, **5.** 185, 1862) has shown that the presence of hydrochloric acid is an essential factor in the complete reduction of selenium salts.

[4] Platinum crucibles are attacked by certain selenides. The crucible must be selected according to the nature of the material under investigation and the constituents to be sought. For selenium only, a porcelain crucible can be used. A nickel crucible with sodium peroxide fusions may also be used.

[5] If a soluble alkaline selenate be in question, the fusion, of course, is not needed.

[6] If the solution contains nitric acid, this must be removed by repeated evaporation with concentrated hydrochloric acid (page 427).

[7] No appreciable loss of selenium will occur if the solution contains sodium or potassium chlorides (B. Rathke, *Liebig's Ann.*, **152.** 194, 206, 1869; *Journ. prakt. Chem.* (1), **108.** 249, 1869; *Zeit. anal. Chem.*, **9.** 484, 1870). One of these salts is also necessary, if the filtrate be evaporated and boiled with hydrochloric acid, in order to make sure that all the selenium is precipitated.

[8] H. Rose, *Pogg. Ann.*, **113.** 472, 1861; *Zeit. anal. Chem.*, **1.** 73, 1862. Sodium or ammonium bisulphite may also be used. A. W. Peirce (*Amer. J. Science* (4), **1.** 416, 1896) reduces selenium with a mixture of potassium iodide and hydrochloric acid. The reduction is more rapid than with sulphur dioxide, and a second reduction of the filtrate is not necessary. For a volumetric process based on this reaction, see J. F. Norris and H. Fay, *Amer. Chem. Journ.*, **18.** 703, 1896; **23.** 119, 1901; P. Klason and H. Mellquist, *Arkiv Kem. Min. Geol.*, **4.** xviii. 1, 1911; *ib.*, **4.** xxix. 1, 1912. The thiosulphate titration fails if arsenic be present because sodium thiosulphate is oxidised by arsenic acid.

[9] According to Rose (*l.c.*), solutions of selenious acid cannot be heated above 100° without appreciable loss of selenium by volatilisation. In the case of nitric acid solutions, the removal of nitric acid by evaporation on a water bath as recommended by Rose (*l.c.*; E. Divers and M. Schimose, *Journ. Chem. Soc.*, **57.** 439, 1890; P. Michaelis, *Ber.*, **30.** 2827, 1897; R. E. Lyons and F. L. Shinn, *Journ. Amer. Chem. Soc.*, **24.** 1087, 1902) leads to low results. Boiling in a reflux condenser with concentrated hydrochloric acid, in order to remove the nitric acid, is not successful even after boiling for 6 hours. Lyons and Shinn add a quarter as much silver or zinc nitrate as is sufficient to combine with the selenium. The selenite so formed is stable at

The following numbers represent the type of results which can be obtained with this process in the presence of a large excess of copper sulphate:

Se used .	0·0100	0·0100	0·0500	0·0500	0·0100	0·0100	grm.
Se found .	0·0094	0·0096	0·0507	0·0496	0·0103	0·0094	grm.

Effect of the Acidity of the Solution on the Precipitation of Selenium and Tellurium by Sulphur Dioxide.—This method of precipitating selenium—boiling with sulphur dioxide in the presence of hydrochloric acid—separates selenium from all metals not precitated by sulphur dioxide, and also from arsenic, antimony, and tin.[3] If much antimony be present, however, tartaric acid must be added to prevent the separation of antimony oxychloride, unless the solution be very strongly acid. The concentration of the hydrochloric acid needs special attention. There is a maximum and a minimum concentration of the acid between which "best" results can be obtained. Keller's important experiments[4] on this subject show that with hydrochloric acid of specific gravity 1·175, and with solutions containing 0·1000 grm. of tellurium, and also solutions containing 0·1000 grm. selenium, and saturated in the cold with sulphur dioxide, the amounts of selenium and tellurium which separated from solutions of different acidity were as follows:

Table LVIII.—Effect of the Acidity of the Solution on the Precipitation of Selenium and Tellurium by Sulphur Dioxide.

Acidity per cent.	Selenium.	Tellurium.	Acidity per cent.	Selenium.	Tellurium.
0·5	...	total	40	total	total
1	0	0·0761	50	total	total
2	...	0·0525	60	total	total
3	trace	0·0653	65	total	0·0965
5	0·0124	0·0745	70	total	0·0882
8	...	0·0931	75	total	0·0411
10	0·0349	total	80	total	nil
20	0·0935	total	90	total	nil
30	total	total	100	total	nil

100°, and insoluble enough in cold water to enable the precipitate to be washed free from nitric acid and nitrates. Evaporate the solution to dryness. Wash down the sides of the vessel with a little water; evaporate again. Treat the residue with 50 c.c. of dilute ammonia and evaporate the solution to dryness; again add ammonia, and again evaporate to dryness. The double $Ag_2SeO_3.NH_3$ so formed (B. Boutzoureano, *Ann. Chim. Phys.* (6), **18**. 289, 1889) is insoluble in water and stable at 100°. Add water twice, and evaporate after each addition to drive off the ammonia. When cool, take up the residue with hydrochloric acid, filter, wash, reduce the selenium by sulphur dioxide, etc.

[1] G. Pellini (*Gazz. Chim. Ital.*, 33. i. 515, 1903; G. Pellini and E. Spelta, *ib.*, 33. ii. 89, 1903) adds 50 to 100 c.c. of a saturated solution of ammonium tartrate and warms the solution for a couple of hours at 50° to 60° with hydrazine sulphate. Selenium is said to be precipitated, tellurium not precipitated. Collect the precipitate in a Gooch's crucible in the usual manner. The tellurium is precipitated from the filtrate by hydrogen sulphide, etc.

[2] For converting selenium into the dioxide by burning it in a current of oxygen, see P. Klason and H. Mellquist, *Arkiv Kem. Min. Geol.*, 4. xviii. 1, 1911.

[3] Some of the heavy metals may be partially precipitated by sulphur dioxide.

[4] E. Keller, *l.c.*; C. Alexi, *Ueber die Bestimmung von Selen und Tellur und die Untersuchung von selen- und tellurhaltigen Handelskupfer*, Berlin, 1905.

These numbers are plotted in fig. 148. The left-to-right downwards cross-hatching shows where selenium is wholly precipitated; the right-to-left downwards cross-hatching shows where tellurium is wholly precipitated; and left-to-right and right-to-left cross-hatching shows where both tellurium and selenium were precipitated.

If selenium alone be present, total precipitation occurs if the acidity of the solution exceeds 30 per cent. If both selenium and tellurium be present, tellurium and selenium will be precipitated if the acidity of the solution be kept between 30 and 50 per cent. But outside these limits either selenium or tellurium may be wholly or partially precipitated, according to the strength of the acid. Selenium will alone be precipitated from a mixed solution if the acidity of the solution exceeds 80 per cent.[1] Hence, if selenium be first precipitated from a solution over 80 per cent. acidity, and the solution made up to twice its former volume with water, the tellurium will be precipitated by a repetition of the sulphur dioxide treatment. The tellurium may be filtered off, dried, and weighed in a similar manner to the process described for selenium.[2]

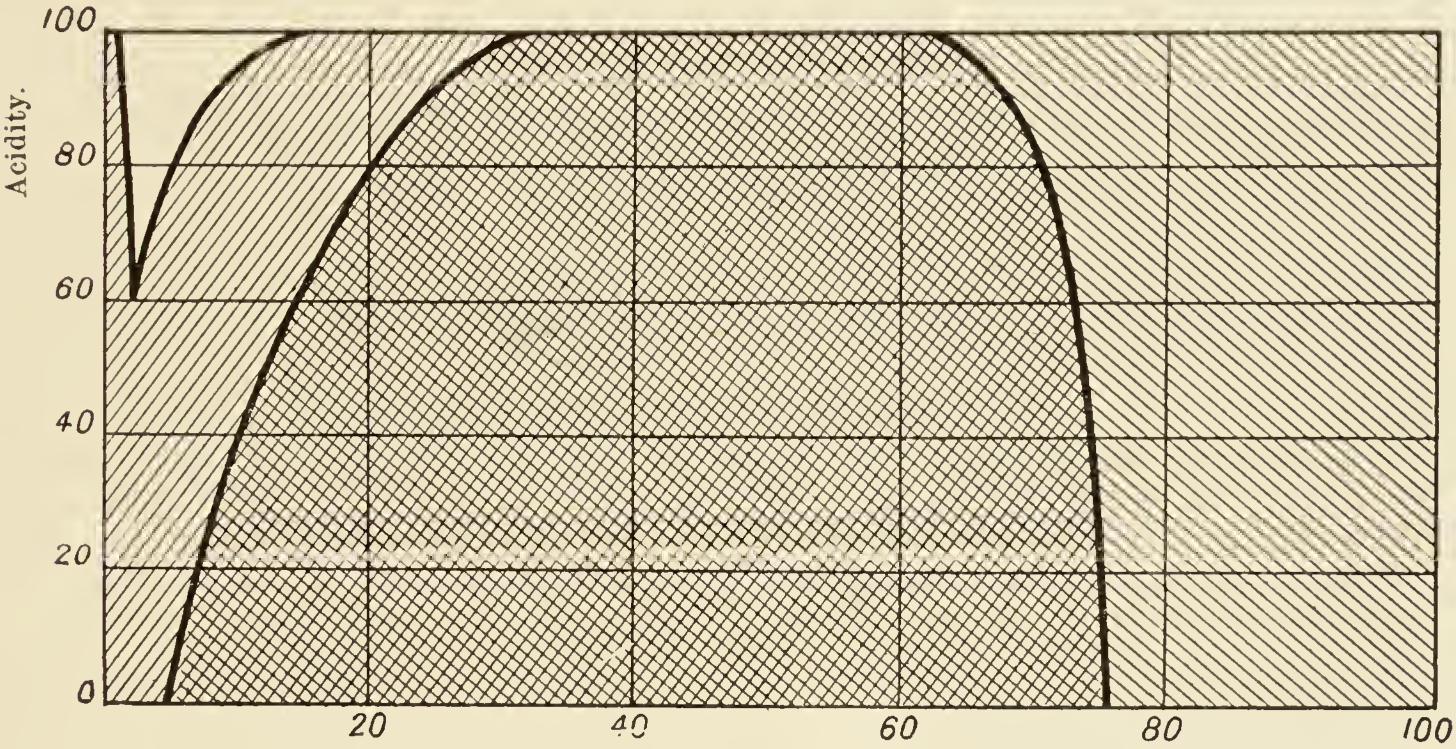

Fig. 148.—Influence of the acidity of the solution on the precipitation of selenium and tellurium.

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[1] The precipitates are more voluminous from feebly acid solutions than from strongly acid solutions.

[2] For the reduction of tellurium solutions with hydrazine salts, see A. Rosenheim and M. Weinheber, *Zeit. anorg. Chem.*, **69**. 266, 1910; P. Jannasch and M. Müller, *Ber.*, **31**. 2377, 1898; A. Gutbier, *ib.*, **34**. 2724, 1901. For the determination of tellurium in minerals, etc., see C. H. Fulton, *Journ. Amer. Chem. Soc.*, **20**. 586, 1898; E. Keller, *ib.*, **19**. 771, 1897; V. Lehner, *ib.*, **21**. 347, 1899; E. Donath, *Zeit. angew. Chem.*, **3**. 216, 1890; R. W. E. MacIvor, *Chem. News*, **86**. 308, 1902; T. Egleston, *ib.*, **47**. 51, 1883.

CHAPTER XXXII.

THE DETERMINATION OF ALUMINIUM AND BERYLLIUM COMPOUNDS.

§ 229. The Gravimetric Determination of Alumina—Hess and Campbell's Process.

THE errors in the determination of the titanium and iron accumulate on the alumina. So also do the errors arising from an imperfect ignition of the mixed oxides ($Fe_2O_3 \rightarrow Fe_3O_4$), imperfect washings, and imperfect separations. It is therefore interesting to find the magnitude of the error affecting the alumina under the conditions of the analysis by the process just indicated. We have seen that with the clay in question there was an error of $\pm 0{\cdot}07$ per cent. in the determination of the titanic oxide, an error of $\pm 0{\cdot}06$ per cent. in the determination of the ferric oxide, and an error of $\pm 0{\cdot}13$ per cent. in the determination of the mixed oxides. Consequently the error in the determination of the alumina by difference[1] amounts to about $\pm 0{\cdot}09$ per cent. This is probably not far different from what would be obtained by a direct determination. The error does not multiply up as it did when the alkalies were determined by difference (page 222). The above estimate of the error becomes less favourable, the less the proportion of alumina in the mixed precipitate, and the greater the proportion of ferric oxide and titanic oxide. A small positive error in the determination of the two oxides—iron and titanium—might altogether mask small amounts of alumina. It is therefore desirable to use a direct method for the determination of small amounts of alumina in the presence of large amounts of iron.

Several processes have been suggested for the direct determination of alumina, but most of them are not very satisfactory in general work. The sodium thiosulphate process will be discussed later, when dealing with zirconium (pages 495, 501). Hess and Campbell[2] give a process which promises well. After a critical examination of the method, Allen said that "minute quantities of alumina may be accurately separated from large amounts of iron by this process." It is based on the fact that aluminium hydroxide is quantitatively precipitated from solutions by the addition of phenylhydrazine. Any phosphorus which might be present will be precipitated with the aluminium hydroxide as aluminium phosphate. Chromium,[3] titanium, zirconium,[4] and thorium,[5] if present, will be precipitated with the aluminium hydroxide; but neither ferrous iron,[1] beryllium,[2] manganese, zinc, cobalt, nickel, cadmium, mercury, magnesia, barium, strontium, nor calcium will be precipitated.[3]

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[1] For the methods of calculation, see J. W. Mellor, *Higher Mathematics*, London, 528, 1909.

[2] W. H. Hess and E. D. Campbell, *Chem. News*, **81**. 158, 1900; *Journ. Amer. Chem. Soc.*, **21**. 776, 1899; E. T. Allen, *ib.*, **25**. 421, 1903; *Chem. News*, **89**. 43, 63, 76, 88, 103, 1904; M. Wunder and N. Chéladzé, *Ann. Chim. anal.*, **16**. 205, 1911.

[3] The precipitation of chromium is slowest in chloride solutions, and quickest in nitrate and sulphate solutions.

[4] A. M. Jefferson (*Journ. Amer. Chem. Soc.*, **24**. 543, 1902) says that zirconium is not precipitated by phenylhydrazine, but Allen shows that this is a mistake.

[5] Thorium is precipitated completely from nitrate solutions, cerium only partially. Titanium and zirconium can be separated from beryllium in chloride solutions by this precipitant.

First Precipitation.—The solution is diluted to 100 or 200 c.c., according to the amount of alumina to be precipitated, and heated to about 90°. Ammonia is added until the precipitate formed just redissolves. Add 5 to 20 drops, according to the amount of iron in solution, of a neutral saturated solution of ammonium bisulphite,[4] with constant stirring, until the solution smells strongly of sulphur dioxide.[5] If the solution turns deep red, it is not acid enough. The red colour shows that ferric sulphite is present. In that case, add a few drops of hydrochloric acid, then add ammonia quickly[6] to make the solution neutral as before. Add a couple of drops of dilute hydrochloric acid. Add phenylhydrazine[7] (1 to 3 c.c.), with constant stirring, to the liquid smelling strongly of sulphur dioxide, until all the alumina is precipitated. When the precipitate has become flaky and settles quickly, filter in the usual manner. The filtration should be done quickly, or a brownish scum may form on the surface of the solution and on the sides of the dish. The solution should not stand more than an hour before filtration. The precipitate is generally coloured brown. The colouring agent is not necessarily ferric hydroxide, but rather organic impurities in the precipitating agent. Wash the precipitate with hot water containing dilute phenylhydrazine bisulphite[8] in solution. Continue the washing until the wash-water gives no indication of iron when mixed with a few drops of ammonium sulphide, or no indication of chlorides. Test the filtrate with a couple of drops of phenylhydrazine to make sure that precipitation is complete.

Second Precipitation.—It is best to redissolve the precipitate on the filter paper in hot dilute hydrochloric acid; wash with hot water; neutralise the

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Beryllium is not precipitated from chloride solutions, but a large proportion is precipitated from sulphate solutions, and a trace from nitrate solutions. The method for the separation of aluminium and chromium from beryllium by this process, which naturally here suggests itself, does not work.

[1] Phenylhydrazine is a powerful reducing agent, and it thus plays a double rôle: (1) maintaining the iron in the ferrous condition; and (2) precipitating the alumina. Ferric oxide, it may be added, is partially precipitated by phenylhydrazine. It is necessary to convert the ferric into ferrous salts before adding the phenylhydrazine, because the latter does not reduce ferric salts very rapidly.

[2] In chloride solutions, as indicated in a previous footnote.

[3] If zinc, cobalt, nickel, mercury, or cadmium be present in concentrated solutions, the corresponding hydroxides may be precipitated. Molybdenum salts give a bright red coloration—L. Spiegel and T. A. Maass, *Ber.*, **36**. 512, 1903.

[4] Ammonium Bisulphite Solution.—Pass sulphur dioxide into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. The object of the sulphur dioxide is not only to reduce the iron, but to keep it in the reduced condition so as to prevent its precipitation with the alumina.

[5] Sulphur dioxide is best purchased in "syphons" of the liquefied gas. The "syphons" are a convenient source of sulphur dioxide for analytical work.

[6] If the operation be done slowly, some ferric hydroxide may be formed which does not dissolve readily in the dilute hydrochloric acid.

[7] Phenylhydrazine costs about 5s. 6d. per lb. To prevent a waste, it is best to add 1 or 2 c.c. of phenylhydrazine, and, if no precipitate is formed, add dilute ammonia drop by drop until a precipitate is just visible. Clear this up by adding one drop of acid, and add more phenylhydrazine. If too little phenylhydrazine has been added, a few drops of the filtrate will show the mistake. The phenylhydrazine should be free from foreign organic matters. Tin has been detected in commercial samples. For preservation, see G. Denigés, *Bull. Trav. Soc. Pharm. Bordeaux*, **52**. 513, 1912.

[8] Phenylhydrazine Bisulphite Solution.—Add a cold saturated solution of sulphurous acid gradually to a few cubic centimetres of phenylhydrazine until the precipitate of phenylhydrazine sulphite, first formed, redissolves to a yellow solution. If the odour of sulphur dioxide appears after standing a few minutes, add a few drops of phenylhydrazine to neutralise the sulphur dioxide. This solution keeps indefinitely in a well-stoppered bottle. For use, mix from 5 to 10 c.c. of the solution so prepared with 100 c.c. of hot water.

solution with ammonia; acidulate with a couple of drops of hydrochloric acid (1 : 1); and precipitate the aluminium hydroxide from the small volume of liquid by the addition of, say, 0·5 c.c. of phenylhydrazine. Wash as before.

The Ignition.—The precipitate is dried in a platinum crucible, charred at a low temperature, and ignited at a bright red heat until its weight is constant. A second ignition is always advisable to make sure the weight is really constant. Weigh as alumina—Al_2O_3.

Errors.—Allen found that when aluminium hydroxide is precipitated from pure solutions the results are inclined to be rather low. For example: Used, 0·2500 grm. Al_2O_3; found, 0·2487 grm. Al_2O_3; error, − 0·0013 grm. But the separation of aluminium, titanium, and zirconium from iron, from a solution containing a mixture of all four salts, gave excellent results. Thus:

Used . . .	0·1817	0·1648	0·1059	0·0726	0·0595	grm.
Found . . .	0·1816	0·1654	0·1063	0·0717	0·0603	grm.
Error . . .	− 0·0001	+ 0·0006	+ 0·0004	− 0·0009	+ 0·0008	grm.

If phosphorus be present, it must either be determined on a separate sample, or the ignited alumina fused with sodium carbonate or potassium bisulphate (page 185), and the phosphorus determined as indicated on page 595. If the phosphorus be in excess of that required to form aluminium phosphate—$AlPO_4$—Hess and Campbell recommend the addition of an excess of a solution of aluminium chloride of known strength, and proceeding as indicated above, making due allowance for the extra alumina.

If desired, the alumina and iron may be precipitated with ammonia in the usual manner (page 182), or with the basic acetate process (page 361), and the alumina precipitated as indicated above from the pyrosulphate fusion. The iron can be determined by difference, or precipitated with ammonium sulphide.[1]

§ 230. The Analysis of Bauxite.

An accurate and complete analysis of this mineral can be made by a process similar to that employed for clays. Time may be saved in analyses for commercial work by using, say, Handy's process,[2] which may be regarded as a type of many others. In Handy's process, 1·5 grms. of the finely powdered bauxite, dried at 100°, is mixed with 50 c.c. of acid,[3] in a 300–350 c.c. evaporating basin. Boil the solution until white fumes are evolved, and continue heating the mixture for another 15 minutes. Cool. Add 100 c.c. of water; stir; boil for 10 minutes. The silica is thus dehydrated and precipitated. Filter the solution into a 300-c.c. beaker. Wash the precipitate with water. The filtrate and washings will occupy between 150 and 200 c.c.

The insoluble matter[4] is ignited in a platinum crucible and weighed. Add 3–4 drops of sulphuric acid and about 5 c.c. of hydrofluoric acid. Evaporate slowly to dryness. Ignite and weigh. The loss in weight represents silica. Fuse the residue with a little potassium bisulphate. When all is dissolved, cool. Take up the mass with water, and add the solution to the main solution. Any insoluble residue will be silica, which is filtered off, ignited, and weighed. The weight is added to the previous result for silica. Make the mixed solution up to 300 c.c.

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[1] Along with other metals precipitated by that reagent, if such elements be present.

[2] J. O. Handy, *Journ. Amer. Chem. Soc.*, **18**. 766, 1896; H. Lienau, *Chem. Ztg.*, **27**. 422, 1903; **29**. 1280, 1905; M. Taurel, *Ann. Chim. Anal.*, **9**. 323, 1904. For a rough method of evaluating aluminous minerals, see J. C. y León, *Anales Soc. Espan. Fis. Quim.*, **8**. 281, 1911.

[3] Acid mixture: 100 c.c. of nitric acid (sp. gr. 1·42), 300 c.c. of hydrochloric acid (sp. gr. 1·20), and 600 c.c. of sulphuric acid (sp. gr. 1·18).

[4] According to E. Baud (*Rev. Chim. pure appl.*, **6**. 368, 1903), the residue will contain silica, and in addition titanic oxide, corundum, and a little alumina. These are subsequently brought into solution by the potassium bisulphate fusion, as described in the text.

Divide the 300 c.c. into three portions of 100 c.c. In one, precipitate a mixture of alumina, titanic oxide, and ferric oxide with ammonium chloride and ammonia.[1] The filtrate from this solution is used for the determination of lime (page 213) and magnesia (page 218).[2] The precipitate is washed, ignited, and weighed (page 183). The titanium can be determined, if necessary, by the gravimetric process (page 207). In the second 100 c.c., determine the iron by reduction with zinc and the permanganate titration (page 187).[3] The alkalies are determined by Smith's process (page 222); the loss on ignition (organic matter and water), as on page 157.

§ 231. The Analysis of Alumina—Hydrated and Calcined.

The alumina "hydrate" on the market may have from about 40 to 65 per cent. of Al_2O_3. It is sometimes sold with a guarantee of 60 per cent. Al_2O_3. The loss on ignition (page 157) includes water and carbon dioxide. For the silica, heat 5 grms. of the hydrate with 25 c.c. of sulphuric acid (sp. gr. 1·4). The alumina dissolves. Cool. Add 100 c.c. of water and boil. The insoluble silica separates. Filter, wash, and ignite the insoluble matter. Fuse the residue with a little potassium bisulphate. Take up the cold mass with water. Filter, wash, ignite in a platinum crucible, and weigh. Treat the mass with sulphuric and hydrofluoric acids as described above. Weigh again. The loss in weight represents silica. Fuse the mass with potassium bisulphate, take up with water, and add it to the main solution. The iron can be determined colorimetrically in this solution (page 200).

The sodium can be determined (1) in the hydrochloric acid solution of the hydrate by the method indicated page 239; or (2) use Smith's process (page 222); or, better still, (3) the sodium can also be determined by calcining 5 grms. of the "hydrate" at a red heat,[4] and digesting the calcined mass on a water bath with an excess of N-H_2SO_4, and titrating back with N-NaOH (page 70). This gives the "total sodium." The "soluble sodium" is determined by boiling 5 grms. of the "hydrate" in water and titrating the filtered solution with N-H_2SO_4, using phenolphthalein as indicator. The difference between the "total" and the "soluble" sodium represents the "combined" sodium. Calculate the soluble sodium to per cent. CO_2, and subtract the result from the percentage loss on ignition. The difference represents water. The alumina is usually determined by difference, although it can be determined by precipitation from an aliquot portion of the "main solution" by the method indicated under bauxite.

Calcined alumina[5] may contain 99 per cent. of alumina. Fuse a gram of the dried alumina with, say, 10 grms. of potassium bisulphate. If the molten mass be not clear, add 2 more grams of the flux to the cold mass and fuse again. Dissolve the cold mass in water. Filter off the insoluble residue and fuse it with sodium carbonate. Take up the cold mass with water in a 300-c.c. evaporating basin. Add 25 c.c. of sulphuric acid, and, when all action has subsided, evaporate the solution until the sulphuric acid begins to fume. Cool; add 100 c.c. of water. Boil the solution. Filter, wash, ignite, and weigh the residue. Treat the residue with sulphuric acid and hydrofluoric acid as described under bauxite. Ignite, and weigh again. The loss represents silica. For sodium, use Smith's process. The alumina is generally determined by difference. These methods will suffice to demonstrate adulterations with china clay or ground flint.

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[1] This method will give low results if a great excess of ammonium chloride be not employed (page 181). The sample can be fused with sodium carbonate, or sodium peroxide, and the cake taken up with dilute hydrochloric acid.

[2] K. W. Jurich, *Die Fabrikation von schwefelsaurer Tonerde*, Berlin, 45, 1894.

[3] There is the difficulty with permanganate titrations mentioned on page 189, when much titanium is present. In that case special precautions must be adopted (see page 190).

[4] This is to make the alumina insoluble in acid.

[5] Alundum is made by fusing bauxite in the electric furnace. It contains about 1 per cent. of silica, ferric and titanic oxides. Alundum is scarcely attacked by aqueous acids and alkalies, and it is but superficially attacked by fused alkaline carbonates.

§ 232. The Analysis of Cryolite.

Silica.—Although cryolite contains a large amount of fluorine, the relatively small amount of silica, which is also present, does not all react with the fluorine, to form volatile silicon fluoride, when the powdered mineral is digested with sulphuric acid. Part remains with the residue undecomposed. This fact makes the determination a little laborious. The silica must be sought both in the residue and in the escaping gases. The solutions cannot be acidified with hydrochloric acid and evaporated in the usual manner, because some silica would be then lost as silicon fluoride. Fresenius and Hintz[1] recommend a process which certainly has not the merit of simplicity. The method indicated on page 637 may be here employed. Fuse the cryolite with an excess of sodium carbonate, and extract the melt with water.[2] Precipitate silica, alumina, lime, etc., with Seemann's solution, and determine the silica, etc., as indicated on page 640.[3] For the sodium, use Smith's process (page 222). The processes indicated on pages 642 and 646 are available for fluorine.

§ 233. The Detection of Beryllium.

If beryllia be present, it will invariably be found associated with the alumina and ferric oxide precipitated by ammonia. The properties of beryllia are closely related to those of alumina. In testing for beryllium,[4] the silica is separated by evaporation, and the hydrogen sulphide group precipitated in acid solution in the usual manner. The filtrate is evaporated down to about 25 c.c., and, when *cold*, add a couple of grams of sodium peroxide (solid). Boil and filter the alkaline solution; acidify the filtrate with nitric acid; and add an excess of ammonia. If no precipitate be formed, beryllium is absent; if a precipitate be formed, transfer it to a small beaker containing 2 or 3 grms. of solid sodium bicarbonate per 20 c.c. of liquid (10 per cent. solution). Raise the temperature rapidly to boiling, and boil half a minute. Alumina is precipitated. Filter. Dilute the filtrate with 10 volumes of water (so as to make approximately a 1 per cent. solution) and boil. If beryllium be present, a precipitate will be formed.

To distinguish beryllia from alumina, dissolve the precipitate in acid[5]; nearly neutralise the solution with ammonia; add ammonium carbonate. The white precipitate may be either aluminium or beryllium hydroxide. The latter alone is soluble in an excess of the reagent, and a white precipitate of basic carbonate is obtained on boiling the clear solution.[1] Again, both aluminium and beryllium salts give white precipitates with caustic soda; with both, the precipitates are soluble in an excess of the reagent; but the solution with beryllia alone gives a white precipitate on boiling the solution. Beryllium, by the way, is sometimes called "glucinum" and symbolised Gl.

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[1] C. R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **28**. 324, 1889.

[2] E. C. Uhlig (*Chemical Analysis for Glassmakers*, Pittsburg, 80, 1903) recommends fusing the cryolite with sodium carbonate as if it were a typical silicate. He ignores the action of the fluorides on the porcelain basin, on the precipitation of alumina (page 180), and the volatilisation of silica as silicon fluoride.

[3] The filtrate is used for the fluorine determination (page 637).

[4] C. L. Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 6, 1908.

[5] Freshly precipitated beryllium hydroxide is readily soluble in potassium or ammonium carbonate, sodium hydroxide, or dilute acids. If the hydroxide be allowed to stand for some time at ordinary temperatures, or if it be heated with water, dilute ammonia, alkaline carbonates, or alkaline hydroxides, the hydroxide appears to become very sparingly soluble in these menstrua.—F. Haber and G. van Oordt, *Zeit. anorg. Chem.*, **38**. 377, 1904.

§ 234. The Gravimetric Determination of Beryllium—Parsons and Barnes' Process.

When beryllium is present, two points require special attention in the treatment of the ammonia precipitate:—(1) When the precipitate is washed with water, and the ammonium chloride has nearly all gone, the beryllium hydroxide begins to pass through the paper, and this more rapidly than is the case with alumina under similar conditions. The addition of ammonium salts—say ammonium acetate—to the water used for washing effectively prevents this action, and the washing then presents no difficulty of this nature. (2) Small amounts of beryllium hydroxide may adhere very tenaciously to the walls of the vessel in which the precipitation is made.[2] Hence, after as much beryllia has been removed as is convenient, it is advisable to wash the walls with a little dilute nitric acid, and re-precipitate the beryllia which has been dissolved.

The beryllia found in the ammonia precipitate along with, say, iron, chromium, and aluminium oxides can be separated by fusing the precipitate for two or three hours with sodium carbonate; the beryllia remains with the iron on washing with water, while the aluminium and chromium pass into solution as aluminates and chromates. The beryllia and iron can be separated by fusion with sodium pyrosulphate, leaching with water, and precipitating the iron with potassium hydroxide. The precipitate is filtered and washed; the filtrate is acidified with hydrochloric acid, and the beryllia precipitated by ammonia.[3]

Parsons and Barnes'[4] process for the quantitative separation of beryllium is based on the insolubility of aluminium and ferric hydroxides in a 10 per cent. solution of sodium bicarbonate, and the ready solubility of beryllium hydroxide[5] in the same reagent.

First Precipitation of Aluminium and Iron.—After the first precipitation by ammonia,[6] the hydroxides are dissolved in hydrochloric acid, and oxidised, if necessary, with a drop of hydrogen peroxide or nitric acid.[7] Neutralise the solution with ammonia, and to the *cold* solution add 10 grms. of solid sodium bicarbonate[1] per 100 c.c. of solution. Cover the beaker[2] with a clock-glass, and heat the solution to boiling as quickly as possible.[3] Boil the solution one minute.[4] Place the beaker in cold water, and, when cold, filter. Collect the filtrate in a litre beaker, and wash the residue three times with a hot (70°–80°) 10 per cent. solution of sodium bicarbonate.

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[1] M. Wunder and N. Chéladzé, *Ann. Chim. Anal.*, **16.** 205, 1911.

[2] B. Bleyer and K. Boshart (*Zeit. anal. Chem.*, **151.** 748, 1912) study the precipitation of beryllium by ammonia and by ammonium sulphide in ordinary glass, in Jena glass, in porcelain, and in platinum vessels. The two last-named gave the best results.

[3] M. Wunder and P. Wenger, *Zeit. anal. Chem.*, **51.** 470, 1912.

[4] C. L. Parsons and S. K. Barnes, *Journ. Amer. Chem. Soc.*, **28.** 1589, 1906; S. L. Penfield and D. N. Harper, *Amer. J. Science* (3), **32.** 112, 1886; *Chem. News*, **54.** 90, 102, 1886; F. A. Gooch and F. S. Havens, *Zeit. anorg. Chem.*, **13.** 435, 1896; F. S. Havens, *ib.*, **16.** 15, 1897; L. A. Aars, *Ueber die analytische Bestimmung von Beryllium und den sogenannten selten Erden*, Kristiania, 1905.

[5] Uranium, if present, also dissolves.

[6] In the case of the basic acetate separation, C. L. Parsons (*Journ. Amer. Chem. Soc.*, **26.** 738, 1904; C. L. Parsons and W. O. Robinson, *ib.*, **28.** 555, 1906) proposes to separate beryllium from iron and aluminium by digesting the mixed precipitate in hot glacial acetic acid, which dissolves basic beryllium acetate from the dried precipitate, and, after filtering the solution through a hot-water funnel, basic beryllium acetate separates from the solution on cooling. The small amounts of ferric and aluminium acetates which dissolve, do not separate on cooling. F. Haber and G. van Oordt (*Zeit. anorg. Chem.*, **40.** 465, 1904) propose to separate beryllium from the mixed basic acetate by treatment with chloroform, in which the basic beryllium acetate dissolves.

[7] Although hydrogen peroxide is usually a better oxidising agent than nitric acid, it is far more likely to introduce impurities into the solution, owing to the greater purity of "commercial nitric acid." Merck's "perhydrol" is the best form of hydrogen peroxide; it is quite pure enough.

Second Precipitation of Aluminium and Iron.—The precipitated ferric and aluminium hydroxides generally retain a little beryllium.[5] Hence, the precipitate is re-dissolved in as little dilute hydrochloric acid (1 : 1) as possible. Collect the filtrate in the same beaker in which the precipitation was first made. Make the solution up to about 100 c.c., neutralise with ammonia, and treat the mixture as the first one was treated.[6] Collect the filtrate and washings in the same litre beaker.

Third Precipitation of Aluminium and Iron.—It is impracticable to wash the sodium bicarbonate from the precipitated ferric and aluminium hydroxides; hence, it is best to again dissolve the precipitate in dilute hydrochloric acid and re-precipitate the iron and aluminium hydroxides with ammonia in the ordinary manner (page 182).

Precipitation of Beryllium.—The joint filtrates from the two precipitations are carefully acidified with concentrated hydrochloric acid with the beaker covered so as to avoid "spurting losses" by the escaping gas.[7] Boil the solution to remove carbon dioxide.[8] Add a slight excess of ammonia, boil, let the precipitate settle, filter, wash with ammonium acetate (2 per cent. solution) until the washings are free from chlorides. Ignite, and weigh as beryllium oxide—BeO.

The Accuracy of the Separation.—In illustration of the accuracy of the method of separation, Parsons and Barnes quote the following separations with mixtures of varying proportions of ferric, aluminium, and beryllium chlorides when the two former were several times the amount of the latter:

Used	0·2152	0·0911	0·0825	0·1020	grm. BeO.
Found	0·2146	0·0906	0·0806	0·0995	grm. BeO.

Hence, the "separation is almost complete. The resulting beryllia was found to be analytically pure." Consequently, the method of separation just described "leaves little to be desired."

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[1] Free from all but traces of sodium carbonate as shown by the phenolphthalein test—page 62.

[2] When the solution is warmed, loss by spitting may occur, if the beaker be not covered.

[3] If too much carbon dioxide be lost on boiling, aluminium may pass into solution.

[4] The brisk evolution of carbon dioxide must not be mistaken for boiling.

[5] And uranium, if present.

[6] A cloudiness in the filtrate is probably due to the dilution of the concentrated solution of sodium bicarbonate with water.

[7] Just before neutralisation, some beryllium may be precipitated, but this redissolves on adding more acid.

[8] Otherwise ammonium carbonate may be formed later on. Beryllium hydroxide is soluble in ammonium carbonate solutions.

CHAPTER XXXIII.

SPECIAL METHODS FOR IRON COMPOUNDS.

"When Nature takes up the brush, iron is almost always on the palette."—R. J. Haüy.

§ 235. The Volumetric Determination of Iron in Hydrochloric Acid Solutions—Reinhardt's Process.

Iron compounds are so common as components of colours, and the effects of iron are so important in the silicate industries, that it is necessary to indicate some alternative methods of analysis other than those described on pages 187 *et seq.* It has been shown that the permanganate titration is useless in the presence of organic matter,[1] and of much hydrochloric acid, unless special precautions be taken. In the latter case, because of the disturbing effects of a side reaction, probably indicated by the equation:

$$16HCl + 2KMnO_4 = 4Cl_2 + 2MnCl_3 + 2KCl + 8H_2O.$$

The chlorine acts as an oxidising agent and furnishes high results (page 194). This effect was pointed out by Löwenthal and Lenssen[2] in 1863. Kessler[3] showed that the presence of manganese sulphate inhibits the side reaction; and Zimmermann[4] further proved that satisfactory results can be obtained in the presence of hydrochloric acid, provided sufficient manganese sulphate be present.

Action of Manganous Sulphate.—According to Manchot,[5] the first action of the permanganate in the titration of a ferrous salt is to form what he calls a "primary oxide"—probably Fe_2O_5. In symbols:

$$Mn_2O_7 + 2FeO = Fe_2O_5 + 2MnO_2.$$

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[1] Ferric salts in the presence of organic matter may be treated by adding a little copper sulphate as catalytic agent, and titrating the solution with standard thiosulphate until a drop gives no red coloration with ammonium thiocyanate.—J. T. Hewitt and G. R. Mann, *Analyst*, **37**. 179, 1912.

[2] J. Löwenthal and E. Lenssen, *Pogg. Ann.*, **118**. 41, 1863; **119**. 225, 1863; *Zeit. anal. Chem*, **1**. 329, 1862; E. Lenssen, *ib.*, **2**. 169, 1863; R. Fresenius, *ib.*, **1**. 361, 1862; H. Kinder, *Stahl Eisen*, **27**. 344, 1907; **28**. 508, 1908; P. Lehnering, *ib.*, **27**. 202, 601, 1907; A. Müller, *ib.*, **26**. 147, 1906; **27**. 204, 1907; H. Wdowiszewski, *Zeit. anal. Chem.*, **42**. 183, 1903; H. Weber, *ib.*, **46**. 788, 1907; **47**. 249, 1908; J. Brown, *Chem. News*, **93**. 59, 1906; *Amer. J. Science* (4), **19**. 31, 1905.

[3] F. Kessler, *Pogg. Ann.*, **118**. 17, 1863; **119**. 218, 1863; *Zeit. anal. Chem.*, **2**. 280, 1863; **21**. 219, 1882.

[4] C. Zimmermann, *Ber.*, **14**. 779, 1881; *Liebig's Ann.*, **213**. 305, 1882; H. P. Cady and A. P. Ruediger, *Journ. Amer. Chem. Soc.*, **19**. 575, 1897 ($HgSO_4$); C. T. Hood, *Chem. News*, **50**. 278, 1884 ($MgSO_4$); J. Krutwig and A. Cocheteux, *Ber.*, **16**. 1534, 1883; *Chem. News*, **48**. 102, 1884; N. W. Thomas, *Amer. Chem. Journ.*, **4**. 359, 1882. H. Rose (*Handbuch der analytischen Chemie*, Braunschweig, **2**. 926, 1871) says that potassium fluoride and potassium sulphate inhibit the reaction; O. Follenius (*Zeit. anal. Chem.*, **11**. 177, 1872) denies this.

[5] W. Manchot, *Liebig's Ann*, **325**. 105, 1902; J. Volhard, *ib.*, **198**. 337, 1879; A. Skrabal, *Zeit. anal. Chem.*, **42**. 359, 1903.

The manganese peroxide so formed oxidises the ferrous salt to a ferric salt. In symbols:

$$MnO_2 + 2FeO = Fe_2O_3 + MnO.$$

In the presence of a sufficient amount of manganous salt, the ferric "primary oxide"—Fe_2O_5—oxidises the manganous oxide—MnO—back to MnO_2:

$$Fe_2O_5 + 2MnO = Fe_2O_3 + 2MnO_2.$$

On the other hand, if but little manganous oxide be present in the solution, and hydrochloric acid is also present, the latter is oxidised by the "primary oxide." In symbols:

$$Fe_2O_5 + 10HCl = 2FeCl_3 + 5H_2O + 2Cl_2.$$

"According to this theory," says Manchot,[1] "the manganese salt acts in two ways. In the first place, it modifies the velocity of the reaction between the ferrous oxide and the permanganate; since, according to Volhard, the permanganate first reacts with the manganese salt to form manganese peroxide, which, in turn, reacts with the ferrous salt. In the second place, the manganous salt 'carries' oxygen from the ferric 'primary oxide'—Fe_2O_5—and gives it up to the unoxidised ferrous salt. In both cases, it is essential that the manganese peroxide shall not react rapidly with the hydrochloric acid, and that the quantity of manganous salt shall not exceed the amount of iron present in the solution." Whatever be the right explanation of the action, the ill effects of the hydrochloric acid are counteracted when a manganous salt is present in suitable proportions, and the amount of hydrochloric acid is not too great.

The Action of Phosphoric Acid.—The presence of ferric chloride in the solution interferes with the end point, on account of the yellow colour of this salt which is formed during the titration. This difficulty was overcome by Reinhardt,[2] who showed that in the presence of phosphoric acid the solution remains colourless until the pink colour of the permanganate appears. This is probably due to the formation of a colourless iron phosphate.

Some contradictory statements have been published as to the efficiency of the subjoined Reinhardt's method[3] of conducting the permanganate titration in the presence of hydrochloric acid, but it can be made to furnish results as consistent as the best volumetric methods, provided a uniform and favourable procedure be adopted. In rapid routine work, where the titanic oxide is neglected,[4] the solution obtained after filtering off the silica may be divided into two equal portions—say 100 c.c. each. In one, the iron and alumina are precipitated in the usual manner; in the other portion, the iron can be determined by the permanganate titration in the following manner:—

The Reduction of Ferric Salts by Stannous Chloride.[5]—The amount of hydrochloric acid in the 100 c.c. under investigation should not exceed 4N-HCl.

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[1] For the theory of induced reactions, see J. W. Mellor, *Chemical Statics and Dynamics*, London, 315, 333, 1904.

[2] C. Reinhardt, *Stahl Eisen*, **4.** 704, 1889; *Chem. Ztg.*, **13.** 323, 1889; *Zeit. anal. Chem.*, **36.** 794, 1897.

[3] L. Brandt, *Chem. Ztg.*, **32.** 812, 830, 840, 851, 1908; C. T. Mixter and H. W. Dubois, *Journ. Amer. Chem. Soc.*, **17.** 405, 1895; G. P. Baxter and J. E. Zanetti, *Amer. Chem. Journ.*, **33.** 500, 1904; G. P. Baxter and H. L. Frevert, *ib.*, **34.** 109, 1905; F. W. Harrison and F. M. Perkin, *Analyst*, **33.** 47, 1908; G. C. Jones and J. H. Jeffery, *ib.*, **34.** 304, 1909; J. A. N. Friend, *Journ. Chem. Soc.*, **95.** 1228, 1909; W. C. Birch. *Chem. News*, **99.** 61, 73, 1909; F. A. Gooch and C. A. Peters, *ib.*, **80.** 78, 91, 1899; *Amer. J. Science* (4), **7.** 461, 1899; M. Wunder and A. Stoicoff, *Ann. Chim. Anal.*, **17.** 361, 1912.

[4] If titanium is to be determined, reserve an aliquot portion of the solution for that purpose.

[5] Ferric chloride solutions can be reduced by amalgamated zinc—D. L. Randall, *Zeit. anorg. Chem.*, **48.** 389, 1906.

Heat the solution to boiling, add a solution of stannous chloride[1] gradually, drop by drop, with constant stirring, until all the ferric chloride is reduced to ferrous chloride.[2] It is important to add as little stannous chloride as possible in excess of that required to reduce the iron.[3] The difficulties incidental to this method of reduction are: (1) the danger of adding insufficient stannous chloride; and (2) the tendency to add too much. If much iron be present, the colour is a fair guide when the reduction is nearly complete; but when the colour is very faint, the stannous chloride is added until a drop of the solution brought quickly into contact with a drop of ammonium thiocyanate solution on a white tile gives no red coloration. When the solution is cold, add rapidly 5 c.c. of a solution of mercuric chloride[4] in order to destroy the excess of stannous chloride. If no precipitate forms, sufficient stannous chloride was not added, and some ferric chloride has not been reduced; if a grey precipitate forms, too much stannous chloride was added. This reacts with the permanganate, spoiling the titration. If a white precipitate of mercurous chloride is formed, it will do no harm,[5] and the solution, after standing 10 minutes, is ready for titration.

The Titration with Potassium Permanganate.—Wash the ferrous chloride solution into a large 600-c.c. beaker, containing a mixture of 25 c.c. of Reinhardt's solution[6] with about 300 c.c. of distilled water and one drop of the solution of permanganate.[7] Titrate the solution at once with permanganate, which is added gradually, drop by drop, with constant stirring. The calculations, etc., are made as indicated on page 198. The whole determination occupies about 20 or 30 minutes. Amounts of copper less than 0·01 per cent. may be neglected in ordinary technical analysis. If more than this amount be present, the copper should be removed.[8]

§ 236. The Volumetric Determination of Iron—Penny's Dichromate Process.

Instead of titrating for iron, in hydrochloric acid solutions, with potassium permanganate according to Reinhardt's process, Penny's dichromate process[9] is commonly used. The ferrous salt is here oxidised with potassium dichromate instead of potassium permanganate. The presence of hydrochloric acid[10] does no particular harm, although the end point is a little sharper with sulphuric than with hydrochloric acid. The end point is not so easily determined in the dichromate process, because a "spot" indicator must be used.[1] Hence, it is easy to "over-titrate." The process is not quite so exact as the permanganate process; but, with practice, there is little to choose between the two so far as accuracy is concerned.

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[1] STANNOUS CHLORIDE SOLUTION.—Dissolve 29 grms. of crystalline $SnCl_2$ in 330 c.c. of concentrated hydrochloric acid, and make the solution up to a litre with water. Add granulated tin and boil the solution until it is clear and colourless. Preserve the solution in a well-stoppered bottle. Some keep a stick of metallic tin in the stoppered bottle with the stock solution. 1 c.c. of the stannous chloride solution will reduce about 0·015 grm. of ferric chloride.

[2] Titanium chloride is not reduced by stannous chloride in hot or cold solutions, and hence the iron determination is not affected by the presence of titanium.

[3] W. F. Stock and W. E. Jack, *Chem. News*, **31**. 63, 1875; **30**. 221, 1874.

[4] MERCURIC CHLORIDE SOLUTION.—A saturated solution containing 50 to 60 grms. per litre. 1 c.c. of the mercuric chloride will oxidise 1·2 c.c. of the stannous chloride solution.

[5] The mercurous chloride is not affected by potassium dichromate (Kessler), nor by potassium permanganate (Reinhardt). For the action of mercurous chloride on ferric salts ($HgCl + FeCl_3 = HgCl_2 + FeCl_2$) see C. Meineke, *Zeit. öffent. Chem.*, **4**. 433, 1898. Hence the titration should be quickly done, to prevent the mercurous salt standing in contact with the ferric salt longer than is necessary—A. E. Haswell, *Rep. anal. Chem.*, **2**. 841, 1882.

[6] REINHARDT'S SOLUTION.—Dissolve 200 grms. of crystalline manganese sulphate in 1000 c.c. of water; add to this a cold mixture of 400 c.c. of concentrated sulphuric acid (sp. gr. 1·8), 600 c.c. of water, and 1000 c.c. of phosphoric acid (sp. gr. 1·3).

[7] To oxidise traces of organic matter in the water, etc.

[8] K. Schröder, *Zeit. öffent. Chem.*, **14**. 477, 1908.

[9] F. Penny, *Chem. Gaz.*, **8**. 330, 1850; *L'Institut*, **18**. 27, 1850; Schabur, *Sitzber. Akad. Wiss. Wien*, **6**. 396, 1851; F. Kessler, *Zeit. anal. Chem.*, **11**. 249, 1872.

[10] Organic matter decomposes hot or cold solutions as in the case of permanganate, but potassium dichromate is not so much affected as the permanganate. See page 195.

Dissolve 2 grms. of fused potassium dichromate[2] in a litre of water. Standardise this solution by dissolving 15·9716 grms. of Mohr's salt in a litre flask with water and concentrated sulphuric acid. Pipette 25 c.c. of this solution into a beaker, and charge the burette with the solution of potassium dichromate. Place 10 or 12 drops of a freshly prepared solution of potassium ferricyanide[3] (1 : 100) separately as spots on a white tile.[4] At intervals during the titration, remove a drop of the solution undergoing titration on a glass rod and mix it with one of the drops on the tile—"spot test." A blue coloration shows that the reaction is not complete and that the solution still contains ferrous iron. When a drop of the solution gives no sign of a blue coloration, the titration is complete. If a drop of the solution being titrated be touched against the side of a drop of the potassium ferricyanide, a little practice will enable one to judge when the end of the reaction is near.[5] The reaction is represented by the equation:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O.$$

Zinc is objectionable as a reducing agent for the dichromate titrations, because the zinc ferricyanide formed in the "spot test" interferes with the indicator. Reductions for the dichromate titration are usually made with stannous chloride (page 452). The solution reduced with stannous chloride is titrated with the standard dichromate as indicated above. The calculation is obvious.[6]

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[1] A solution of *s*-diphenylcarbazide—$CO(NH.NH.C_6H_5)_2$—in the presence of an excess of hydrochloric acid has been suggested as an internal indicator. This turns violet when the reaction is over. P. Cazeneuve, *Chem. Ztg.*, **24**. 684, 1900; *Bull. Soc. Chim.* (4), **23**. 592, 701, 769, 1900; L. Brandt, *Zeit. anal. Chem.*, **45**. 95, 1906; O. L. Barnebey and S. R. Wilson, *Journ. Amer. Chem. Soc.*, **35**. 156, 1913. The solution of *s*-diphenylcarbazide is prepared by dissolving 0·1 grm. of the carbazide in 35 c.c. of acetic acid and diluting the solution to 100 c.c. Use 5 c.c. as indicator. The solution decomposes if kept very long. 10 grms. will suffice for 2000 titrations. The indicator reduces the standard dichromate, but when a suitable correction is made the results are good.

[2] Potassium Dichromate Solution.—Fuse about 5 grms. of the pure crystallised salt in a platinum crucible below a red heat. The salt fuses in the neighbourhood of 400°. Cool in a desiccator. The fusion must not be made at too high a temperature. R. W. Atkinson (*Chem. News*, **49**. 117, 1884) states that, "however carefully the heat be regulated, on dissolving in water, and allowing to settle, a green deposit of chromic oxide will be found at the bottom of the flask or beaker. This shows that a small amount of decomposition occurs during the fusion, and that the value of the standard must be lower than is theoretically required for the amount of dichromate weighed out."

[3] The ferricyanide should be free from ferrocyanide, which gives a blue coloration with ferric salts. For the disturbing effects of copper, see J. S. Parker, *Chem. News*, **22**. 313, 1870. Potassium ferricyanide will show 1 part of iron in 500,000 parts of water—A. Wagner, *Zeit. anal. Chem.*, **20**. 349, 1881.

[4] Some prefer a slab of paraffin wax, or a white tile covered with a layer of paraffin, owing to the form the drops take on the wax, and the ease in cleaning the waxed slab. R. Seligmann and F. J. Willott, *Journ. Soc. Chem. Ind.*, **24**. 1278, 1905.

[5] The development of the ferricyanide "blue" is slow with dilute solutions of ferrous salts, and the end point may thus be judged prematurely. To get the true end of the reaction, let the mixed drop stand 5 minutes covered with a crucible lid to shut out the light. The reaction is disturbed by elements which form insoluble ferricyanides—the brown colour with manganese, nickel, or copper, for instance, masks the reaction with dilute ferrous solutions. Hence, the ferricyanide is generally made slightly "acid" to prevent the formation of insoluble ferricyanides. H. Vogel (*Chem. News*, **23**. 142, 1871; R. W. Atkinson, *ib.*, **49**. 217, 1884; L. van Itallie, *Pharm. Weekblad*, **40**. 490, 1903) says that 30 seconds' exposure to sunlight is sufficient to make potassium ferricyanide solutions give a blue colour with ferric salts.

[6] For titrating ferric chloride solutions directly with stannous chloride, see page 310, where the converse process is described. For cobalt chloride or cobalt nitrate indicators, see F. P.

§ 237. The Gravimetric Determination of Iron—Ilinsky and Knorre's Process.

Several methods are available for the quantitative precipitation of iron in the presence of aluminium salts.[1] Ilinsky and Knorre's process[2] gives satisfactory results in separating ferric or ferrous iron from aluminium, chromium, manganese, nickel, zirconium, zinc, lead, cadmium, antimony, arsenic, magnesium, calcium, beryllium, but not vanadium, tungsten, copper, and cobalt. Silver, tin, bismuth, as well as molybdenum, interfere with the precipitation of iron, cobalt, vanadium, tungsten, and copper by the nitroso-β-naphthol process. Some phosphorus, if this element be present, will be precipitated with the iron. The following is the method:—

The solution of the chloride or sulphate under investigation is neutralised with sodium carbonate, and acidified with a few drops of hydrochloric acid. The cold solution is stirred with a concentrated acetic solution of nitroso-β-naphthol.[3] A voluminous precipitate of $Fe(C_{10}H_6O.NO)_3$ separates on standing, say, overnight. Try if any more reagent causes any further precipitation in the clear solution. Wash the precipitate with 50 per cent. acetic acid, and finally with cold water.[4] The precipitate is dried and ignited in a capacious crucible,[5] and heated so that the temperature gradually rises. When all the carbon has burned off, the crucible is cooled, and the weight of Fe_2O_3 determined. Trial results on known mixtures of alumina and iron are quite good. If necessary, the organic matter in the filtrate is destroyed by boiling with hydrochloric acid and potassium chlorate.

§ 238. The Gravimetric Determination of Iron—Baudisch's Cupferron Process.

Baudisch[6] has shown that ammonium nitrosophenylhydroxylamine—called for brevity "cupferron" or Baudisch's reagent—promises to be a valuable agent for separating ferric and cupric salts from most other metals—mercury, tin, lead, bismuth, and silver, however, may be partly precipitated with the iron and copper if these elements be present. The precipitated iron and copper salts

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Venable, *Journ. Anal. App. Chem.*, **1**. 312, 1887; A. C. Campbell, *ib.*, **2**. 4, 1888; F. H. Morgan, *ib.*, **2**. 172, 1888.

[1] Trimethylamine precipitates iron in the presence of aluminium and chromium compounds —L. Vignon, *Journ. Pharm. Chim.* (5), **12**. 677, 1885; *Zeit. anal. Chem.*, **26**. 631, 1887. A solution of naphthenic acid in benzene precipitates ferrous oxide in presence of aluminium, etc. K. Charitschkoff, *Chem. Ztg.*, **35**. 463, 671, 1911; E. Pyhälä, *ib.*, **36**. 869, 1912; I. I. Lutshinnskii, *ib.*, **35**. 1204, 1911; E. Pyhälä, *ib.*, **36**. 869, 1913. Pyridine also precipitates iron in the presence of manganese, nickel, and cobalt—R. B. Moore and I. Miller, *Journ. Amer. Chem. Soc.*, **30**. 593, 1908; *Chem. News*, **98**. 105, 1908—and J. A. Sanchez (*Bull. Soc. Chim.* (4), **9**. 880, 1911) recommends the pyridine precipitation for separating iron and manganese. Zinc should be absent, for it is precipitated by pyridine. Hydrazine hydrate also precipitates ferric iron quantitatively—E. Schirm, *Chem. Ztg.*, **35**. 897, 1911.

[2] M. Ilinsky and G. von Knorre, *Ber.*, **18**. 2728, 1885; G. von Knorre, *Zeit. anal. Chem.*, **28**. 234, 1889; *Zeit. angew. Chem.*, **6**. 264, 1893; **17**. 641, 1904; R. Burgass, *ib.*, **9**. 596, 1896; L. L. de Koninck, *Rev. Univ. Mines* (2), **9**. 243, 1890; M. Schleier, *Chem. Ztg.*, **16**. 420, 1892; M. Béard, *Ann. Chim. Anal.*, **10**. 41, 1905.

[3] NITROSO-β-NAPHTHOL SOLUTION.—8 grms. of nitroso-β-naphthol are dissolved in 300 c.c. of glacial acetic acid. The solution is diluted with 300 c.c. of water, and filtered. The solution will keep about a month in a dark place. Nitroso-β-naphthol costs about 8s. per 100 grms.

[4] There is no particular difficulty in washing the precipitate, except its comparatively large volume.

[5] Capacious, because the precipitate swells very much during the earlier stages of the ignition.

[6] O. Baudisch, *Chem. Ztg.*, **33**. 1298, 1909; **35**. 913, 1911; O. Baudisch and V. L. King, *Journ. Ind. Eng. Chem.*, **3**. 629, 1911; H. Biltz and O. Hödtke, *Zeit. anorg. Chem.*, **66**. 426, 1910; H. Biltz and A. Soukup, *ib.*, **68**. 52, 1910; R. Fresenius, *Zeit. anal. Chem.*, **50**. 35, 1911; H. Nissenson, *Zeit. angew. Chem.*, **23**. 969, 1911.

are but slowly attacked by 2N-HCl in the cold; but they are decomposed by hot acid. Cold dilute sodium carbonate has no appreciable action, but the alkaline hydroxides decompose the precipitate rapidly. Ammonia does not affect the iron salt, but it quickly dissolves the copper salt, and it is therefore possible to separate the iron and copper salts by digesting the mixed salts with ammonia, cold. The precipitation is best made in strongly acid (hydrochloric, sulphuric, or acetic[1]) solutions, thus:—

Add 20 c.c. of concentrated hydrochloric acid to 100 c.c. of solution at the room temperature. Add a cold solution of Baudisch's reagent[2] slowly, with constant stirring. A reddish-brown (iron)—or greyish-white (copper)—flocculent precipitate separates. The end of the precipitation is easy to recognise, since small white crystals of nitrosophenyl-hydroxylamine—$C_6H_5(NO)OH$—separate as soon as all the copper or iron has been precipitated. It is then necessary to add a further excess of the reagent, say, one-fifth of the volume of that already added. In about 15 minutes, filter on a paper filter by suction. Wash first with 2N-HCl, then with water, and then with ammonia in the case of iron, and sodium carbonate in the case of copper, so as to remove the excess of the reagent. Finish the washing with water. The precipitate can be ignited very slowly in the ordinary way and weighed as oxide—Fe_2O_3 (or CuO).[3]

Trial separations of iron from aluminium, nickel, chromium, and of copper from zinc and cadmium, are excellent. The chief value of the process lies in the fact that it furnishes a useful means of precipitating iron in the presence of cobalt, zinc, manganese, nickel, chromium, aluminium, alkaline earths, alkalies, phosphates, and sulphates.[4] The separation of copper from cadmium and zinc by this process offers, as yet, no particular advantages over the older process (page 350). It has also been recommended for separating titanium from aluminium.[5]

§ 239. The Separation of Iron—Ether Process.

When a solution of ferric chloride with arsenic, antimony, aluminium, titanium, zirconium, chromium, vanadium, manganese, uranium, cobalt, nickel, copper, calcium, and magnesium chlorides is acidified with hydrochloric acid, and shaken with ether, the mixture separates into two layers—an ethereal solution of ferric chloride above, and an aqueous solution of the other chlorides below. The two layers can be separated in a suitable funnel. Some gold, tungsten, and molybdenum,[6] if present, are more or less completely removed with the iron in the ethereal layer. The same remark applies to thallium, stannous and mercuric chlorides.[7] W. Skey first proposed to separate iron from many associated elements in this manner; and he also suggested the corresponding separations: cobalt from nickel; and gold from platinum.[1] Rothe,[2] however, has applied Skey's idea to the technical analysis of iron compounds, and the method has now won a place in analytical practice. Two or three extractions with ether are sufficient to remove practically all the iron.

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[1] Acetic acid is best for copper.

[2] Baudisch's Cupferron Reagent.—Dissolve 6 grms. of the white crystalline solid—ammonium nitrosophenyl-hydroxylamine—in water and make the solution up to 100 c.c. The solution will keep in the dark for about a week. If exposed to the light, it becomes turbid owing to the formation of nitrobenzene. Old turbid solutions should be filtered before use. The crystalline solid costs about 8s. 9d. per 100 grms.

[3] Finish the ignition with a Winkler's chimney (page 213).

[4] For instance, say, 5 grms. of a brown iron ore are digested with 60 c.c. of concentrated hydrochloric acid, and boiled with potassium chlorate. When cold, make the solution up to 500 c.c. Pipette 25 c.c. into a beaker, add 20 c.c. of hydrochloric acid and 100 c.c. of cold distilled water. Stir in the equivalent of 3 grms. of the cupferron reagent, etc.

[5] I. Bellucci and L. Grassi, *Atti R. Accad. dei Lincei*, *Rome*, **22**. i. 30, 1913.

[6] Molybdenum appears to be but imperfectly separated in the absence of ferric chloride—W. Skey, *Chem. News*, **36**. 48, 1880; **16**. 201, 324, 1867; A. A. Blair, *Journ. Amer. Chem. Soc.*, **30**. 1229, 1908; R. de Jong, *Zeit. anal. Chem.*, **41**. 596, 1902; C. D. Braun, *ib.*, **2**. 36, 1863; **6**. 86, 1867.

[7] The chlorides of the alkalies, calcium, nickel, zinc, and cadmium; and the thiocyanates of nickel, copper, and zinc, are soluble in anhydrous but not in aqueous ether—W. Skey, *Chem. News*, **36**. 48. 1880. Stannous chloride is soluble in ether—M. de Jong, *Zeit. anal. Chem.*, **41**. 596, 1902.

Effect of Acid.—The acidity of the solution requires attention.[3] If the solution has much above or below "20 per cent. HCl," the efficiency of the extraction will be impaired. For instance, Speller found that when 0·8 grm. of iron (as ferric chloride) was dissolved in 100 c.c. of hydrochloric acid, of the strength stated, shaken with twice its volume of ether, and allowed to stand 30 minutes at 17°–18°, the iron was divided between the ethereal and aqueous layers as indicated in Table LVIII.

Table LIX.—Relation between the Strength of the Acid and the Partition of Iron (as Ferric Chloride) between Ether and Dilute Acid.

Strength of hydrochloric acid. (Sp. gr.)	Per cent. of iron.	
	Aqueous solution.	Ethereal solution.
1·193	99·0	1·0
1·164	97·5	2·5
1·158	92·84	7·16
1·151	74	26·0
1·123	7·2	92·8
1·115	2·4	97·6
1·111	2·0	98
1·105	1·95	98·05
1·103	1·95	98·05
1·091	3·3	96·7
1·0825	10·0	90·0
1·069	47·5	52·5
1·06	87·0	13·0
1·0525	98·4	1·6
1·0424	99·6	0·4

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[1] R. Willstätter (*Ber.*, **36**. 1830, 1903) separates gold chloride from platinum chloride in aqueous solutions by extracting with ether—F. Mylius, *Zeit. anorg. Chem.*, **70**. 203, 1911. See page 431.

[2] J. W. Rothe, *Mitt. königl. tech. Ver.*, **10**. 132, 1892; *Chem. News*, **66**. 182, 1892; *Stahl Eisen*, **12**. 1052, 1892; A. Ledebur, *ib.*, **13**. 222, 1893; E. Hanriot, *Bull. Soc. Chim.* (3), **7**. 161, 1892; F. N. Speller, *Chem. News*, **83**. 124, 1901; E. Pinerua, *ib.*, **75**. 193, 1897; A. A. Noyes, W. C. Bray, and E. B. Spear, *Tech. Quart.*, **21**. 14, 1908; *Journ. Amer. Chem. Soc.*, **30**. 481, 1908; G. W. Sargent, *ib.*, **21**. 854, 1899; A. C. Langmuir, *ib.*, **22**. 102, 1900; E. F. Kern, *ib.*, **23**. 685, 1901 (separation of iron from uranium); J. M. Matthews, *Journ. Amer. Chem. Soc.*, **20**. 846, 1898; *Chem. News*, **79**. 97, 112, 1899 (separation of iron from zirconium, thorium, cerium, and titanium); F. A. Gooch and F. S. Havens, *ib.*, **74**. 296, 1896; *Amer. J. Science*, (4), **2**. 416, 1896 (separation iron and aluminium); A. Carnot, *Méthodes d'Analyse des Fontes des Fers et des Aciers*, Paris, 123, 1895. For the separation of iron and vanadium, E. Deiss and H. Leysaht, *Chem. Ztg.*, **35**. 878, 1911; for iron and nickel, J. P. Thompson, *Journ. Ind. Eng. Chem.*, **3**. 950, 1911. G. L. Norris (*Journ. Soc. Chem. Ind.*, **20**. 551, 1901) prefers a mixture of acetone and ether rather than ether alone.

[3] It must be pointed out that, since the ether initially contains no hydrochloric acid, the amount of hydrochloric acid in the aqueous layer is decreased by each extraction if ordinary ether be used. Hence, some use ether slightly acidified with HCl. Ether dissolves 3 per cent. of its volume of water. 10 c.c. of a solution of ether which had been shaken with an equal volume of hydrochloric acid (sp. gr. 1·1033) contained but 0·0019 grm. of HCl. Speller found that when 150 c.c. of anhydrous ether were shaken with 100 c.c. of hydrochloric acid, and allowed to stand 30 minutes between 17–18°, 100 c.c. of the acid contained:

Ether . . .	140	89	64	30	19	15·5	14·4 c.c.
Sp. gr. acid . . .	1·177	1·140	1·123	1·103	1·075	1·063	1·055

The presence of ferric, copper, cobalt, and nickel chlorides in the hydrochloric acid slightly modified the solubility of ether in the acid.

Hence, *hydrochloric acid of specific gravity* 1·100–1·115 (25·5 *grms. of HCl per* 100 *c.c. of solution*) *is most favourable to the extraction of ferric chloride by ether.*

Effect of Phosphorus.—If phosphorus be present, Wysor[1] has shown that there is an increasing amount of phosphorus lost in the ether layer with an increase in the proportion of iron and phosphorus. But "a fairly constant percentage of the phosphorus present in the solution remains with the iron in the ether separation. The approximate error may therefore be calculated and the proper correction applied." The first line in the following table represents the amount of soluble phosphorus pentoxide in the given sample; and the second line, the weight of phosphorus pentoxide to be added to the weight of the Al_2O_3 residue found per gram of iron:

P_2O_5	0·0023	0·0046	0·0092	0·0182	0·0366	grm.
Correction per 1 grm. Fe . .	0·0005	0·0009	0·0016	0·0031	0·0060	,,
Correction per 2 grms. Fe . .	...	0·0015	0·0029	0·0055	0·0108	,,
Correction per 3 grms. Fe . .	...	0·0017	0·0032	0·0064	0·0130	,,

It is assumed that the correction for the intermediate values of phosphorus and iron can be obtained by interpolation.

Extraction of the Iron by Rothe's Pipette.[2]—Rothe's pipette, mounted ready for use, is illustrated in fig. 149. Two mixing cylinders, each about 200 c.c., are connected with a 3-way cock. The other ends of the cylinder are fitted with 2-way stopcocks. The boring of the 3-way cock will be obvious from fig. 150, which shows five different positions, numbered 1 to 5.

The 3-way cock is place in the position No. 1; the solution under investigation,[3] containing about 20 per cent. of hydrochloric acid, and occupying 50–60 c.c., is poured into the left cylinder by means of the long funnel as shown in the diagram, fig. 149. The beaker and funnel are washed with 20–23 per cent. hydrochloric acid. Close the left stopcock. Place the funnel in the other cylinder, and introduce 100 c.c. of ether.[4] Remove the funnel, and close the stopcock. Connect the ether cylinder with the rubber bellows, as shown in the diagram. Open the right stopcock and blow a small quantity of air into the ether cylinder. Turn the 3-way stopcock into the position No. 2, and ether will bubble through the solution into the left cylinder. The ether becomes warm as it mixes with the solution.[5] When about nine-tenths of the ether has bubbled through the solution, restore the 3-way cock to No. 1 position. Close the other two

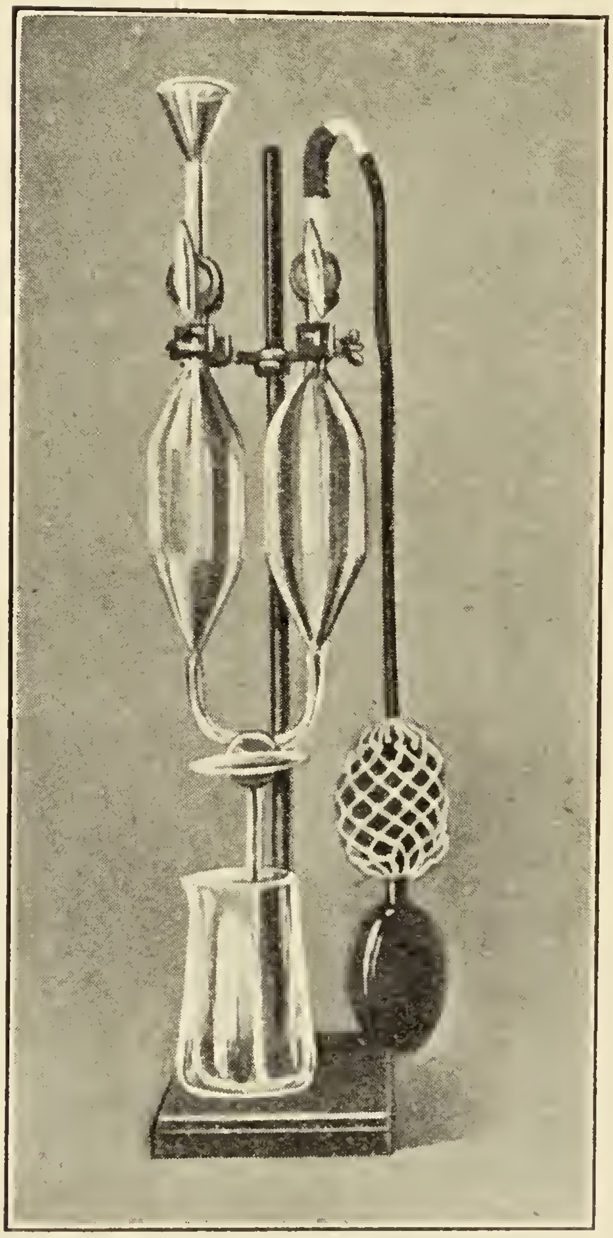

Fig. 149.—Rothe's ether pipette.

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[1] R. J. Wysor, *Journ. Ind. Eng. Chem.*, **2**. 45, 1910.

[2] Many other forms of "separating funnels" or "separating pipettes" have been devised, *e.g.* A. Carnot, *Méthodes d'Analyse des Fontes des Fers et des Aciers*, Paris, 124, 1895.

[3] The solution should be quite clear; if not, filter. Nitric acid and chlorine should be absent. If present, they must be removed by evaporation.

[4] No naked flames must be near while the ether is being used.

Some ferric chloride is reduced to ferrous chloride. But this does not matter.

cocks. Cool the cylinder under a stream of cold water, and thoroughly agitate the solution under the water tap. Open the right cock. Force more air into the right cylinder, and turn the 3-way cock into position No. 2. The remaining ether passes into the left cylinder.[1] Turn the 3-way stopcock into position No. 1. Close the two remaining cocks and shake the apparatus vigorously. Let the apparatus remain at rest two or three minutes. The liquid in the left cylinder separates into two layers. Open the two 2-way stopcocks, and turn the 3-way cock into position No. 2. When the lower aqueous layer has passed into the right cylinder,[2] so that but a little of the aqueous layer remains in the capillary tube on the left, turn the 3-way cock into position No. 1. Close the two 2-way cocks. Shake the cylinder, whereby any drops of aqueous liquid adhering to the walls of the left cylinder collect on the bottom. The ethereal layer will be clear in 5–10 minutes. Then blow the remaining aqueous liquid into the right cylinder until a little of the ethereal layer appears in the capillary at the bottom of the right cylinder. Place a beaker below the 3-way stopcock, and turn this cock into the position No. 3. Open the left 2-way cock, and the ethereal solution containing the $FeCl_3$ flows into the beaker.[3] Turn the 3-way cock into the position No. 1. Pour a little ether into the left cylinder. Close the stopcocks; shake; and if any aqueous solution separates, blow it into the right cylinder and run off the excess ether by turning the 3-way cock into the position No. 3 as before. Turn the 3-way cock into position No. 1. Pour about 50 c.c. of ether into the left cylinder and repeat the preceding operations, simply reversing the cylinders.[4] This leaves the aqueous solution in the left cylinder.

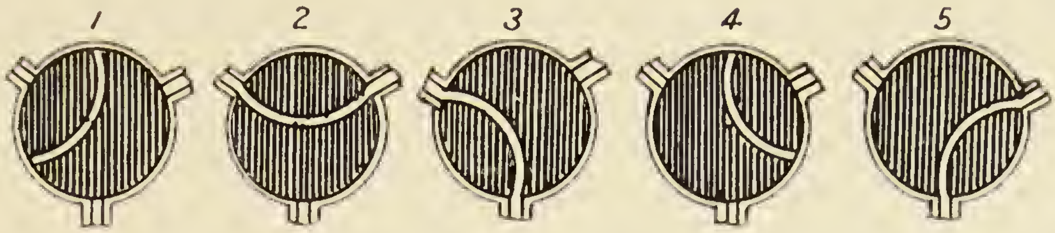

FIG. 150.—Bore of stopcock in Rothe's pipette.

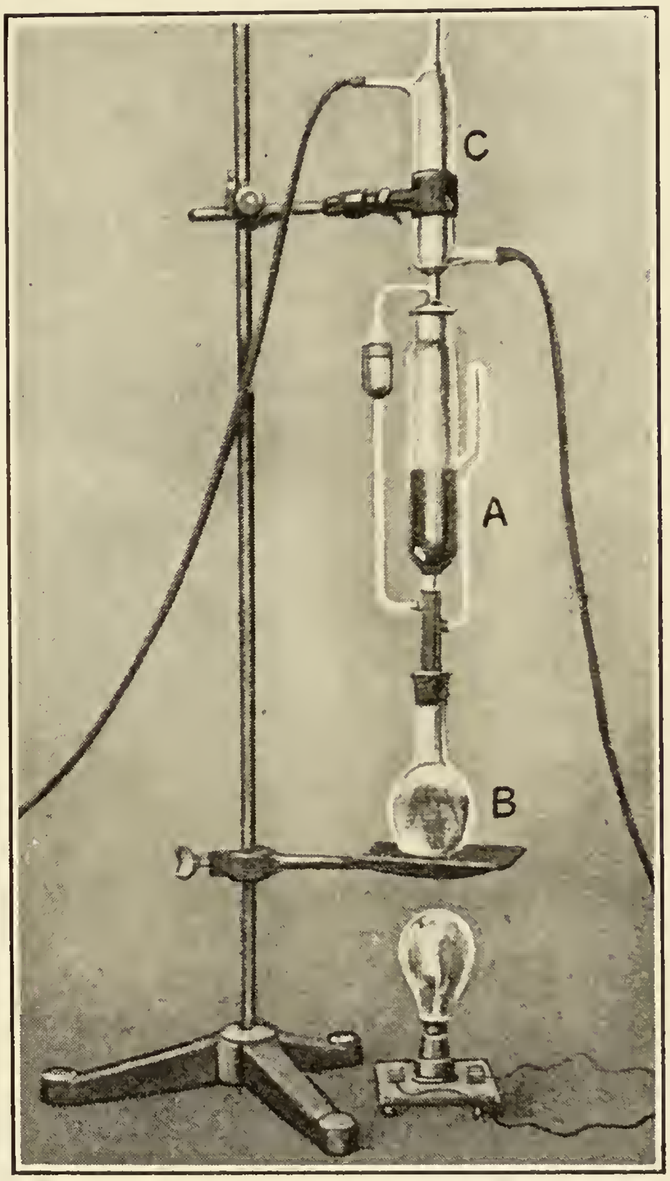

FIG. 151.—Extraction of liquids with ether.

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[1] This procedure prevents error arising from the non-extraction of the liquid in the capillary tubes connecting the two cylinders.

[2] Assisted, if necessary, by connecting the blower with the left cylinder.

[3] If much copper and cobalt be present, appreciable quantities of copper and cobalt chloride will be dissolved by the ether. In that case, add 10 c.c. of hydrochloric acid (sp. gr. 1·104) to the ethereal solution, shake, and draw off the aqueous layer containing the copper and cobalt into a second beaker.

[4] Note the position of the 3-way cock Nos. 4, 2, 5 for working the right cylinder, compared with Nos. 1, 2, 3 while working the left cylinder.

Repeat the operation a third time with another 50 c.c. of ether. This leaves the aqueous solution in the right cylinder.

Treatment of Ethereal Layer.—The three ether extractions have removed practically all the iron from the aqueous layer. The ethereal solution is transferred to a porcelain basin, and evaporated on a water bath, not too hot, in order to drive off the ether, and evaporate to dryness. The residue may then be dissolved in hydrochloric acid and the iron determined in the usual manner (page 198).

Treatment of Aqueous Layer.—The aqueous solution freed from iron is also run off into another porcelain dish. The funnels are washed with 20 per cent. hydrochloric acid, and the solution is evaporated to dryness to remove the ether. It is then ready for any other separations which may be required.

Extraction of the Iron by Soxhlet's Extractor.—Instead of "shaking out" with ether by means of the separating funnel, it may be more convenient to extract the iron from the solution by a modification of Soxhlet's extractor,[1] say Taylor's extractor, illustrated in fig. 151. The solution—25–30 c.c.—is placed in the receptacle *A*; ether is placed in the flask *B*. The latter is heated by a water bath, or an electric lamp. The ether boils, the vapour is condensed in *C*. The condensed liquid runs into *A*, bubbles through the liquid, and is finally syphoned into the flask *B*. This circulation of the ether will extract all the iron from the solution in a short time. At the end of, say, an hour, when the solution has cooled, the apparatus is disconnected. The ethereal solution of iron in the flask *B*, and the extracted solution in the receptacle *A*, are treated as described above.

§ 240. The Analysis of Iron Oxides, Red Earths, and Iron Ores.

The iron in iron ores, iron oxides, and red marls can sometimes be extracted by boiling the powdered sample with concentrated hydrochloric acid—with or without a little nitric acid. Nitric acid should always be added if sulphides be present, in order to oxidise the sulphides to sulphates.[2] The silicate ores are sometimes more easily decomposed by digestion in acids if they be first calcined at a low temperature;[3] and even if the ore dissolves readily in acids, the silica obtained in the subsequent evaporation (page 167) is cleaner and more pure than if the uncalcined ore had been digested directly in acids.[4]

If the sample be not decomposed by digestion in acids, the sodium peroxide fusion may be employed, as described on pages 266 and 475. If iron alone is to be determined, the peroxide fusion is usually quite satisfactory for red clays, calcined iron oxides, etc.; but several alternative methods have been suggested.[5]

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[1] H. P. Smith, *Chem. News*, **83**. 152, 1901; H. Göckel, *Zeit. angew. Chem.*, **10**. 683, 1897.

[2] Otherwise, the results of, say, the bichromate titration will be high. W. F. K. Stock and W. E. Jack, *Chem. News*, **30**. 221, 1874. A. Esilman (*Chem. News*, **30**. 243, 1874) recommends filtering off the insoluble matters before titrating for the iron, in order to eliminate as far as possible the secondary effects of carbonaceous matters, pyrites, etc.

[3] E. Ladd (*Min. Eng. World*, **36**. 1350, 1912) proposes to avoid the fusion in the analysis of china clays by utilising this principle, but the method cannot be recommended. W. H. Worthington (*Min. Science*, **63**. 521, 1911) recommends opening the sample of ore (in the absence of lime and baryta) with potassium bisulphate, because the silica can be filtered immediately the aqueous extract of the cold cake has been boiled in water. Fusion, filtration, and washing of the silica occupy about 30 minutes.

[4] Of course the iron oxides resist attack by the acids better after calcination, but this is not necessarily the case with silicates calcined at, say, dull redness. H. Rocholl, *Zeit. anal. Chem.*, **20**. 289, 1881; G. W. Dean, *Journ. Amer. Chem. Soc.*, **28**. 882, 1906; H. E. Ashley, *Chem. News*, **90**. 274, 1904.

[5] R. W. E. MacIvor (*Chem. News*, **29**. 246, 1874; B. Krieger, *Chem. Ztg.*, **35**. 1054, 1911) states that the iron in hæmatites, etc., readily dissolves as ferrous iron when the finely powdered

The iron, when dissolved, is reduced and determined by titration with permanganate or dichromate.

For a complete analysis, the sodium carbonate fusion (page 164) may be employed. A little sodium nitrite (1 to 1·5 grms.)[1] should be added in order to oxidise the sulphides to sulphates. Care must be taken to heat the mixture slowly, or loss by spurting, etc., may occur. The hygroscopic moisture, combined water, silica,[2] elements precipitated by hydrogen sulphide in acid solution, alumina, iron oxide, phosphoric and titanic oxides are determined as indicated on page 210. The sulphur can be determined in an aliquot portion of the filtrate from the silica; chromium can be determined as indicated on page 469. The filtrate from the basic acetate separation can be used for the determination of manganese, zinc, nickel, cobalt, lime, and magnesia. The zinc is first precipitated as sulphide by hydrogen sulphide in dilute (formic, hydrochloric, etc.) acid solution (page 364). The mixed sulphides of manganese,[3] nickel, and cobalt are then precipitated by hydrogen sulphide in ammoniacal solution as indicated on page 389. The magnesia and lime are determined in the filtrate. The residual mixed sulphides are taken up with aqua regia (page 389); the solution neutralised with sodium carbonate; acidified with acetic acid and treated with hydrogen sulphide, whereby nickel and cobalt sulphides are precipitated, as described on page 389.

§ 241. The Determination of Ferrous Oxide.

Iron existing in the ferrous condition is rarely reported in clay analyses, and when the relative proportions of ferrous and ferric oxides are indicated the results are usually of little or no value. One reason is that no satisfactory general method is known for the determination of the ferrous iron in clays containing organic matter. A number of different methods have been suggested for decomposing silicates without interfering with the state of oxidation of the iron. For example:

(1) Fusion with sodium carbonate. The objection to this process is the risk of absorbing air during the fusion, and the consequent oxidation of the manganese.

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material is digested in a long-necked flask with sulphuric acid and metallic zinc until all the iron is dissolved. The iron is in the ferrous condition ready for titration with potassium permanganate. H. Bornträger (*Zeit. anal. Chem.*, **35.** 170, 1896; **38.** 774, 1899) says that ignited ferric oxide dissolves at once in acid provided a little iron-free manganese dioxide be added. This is probably due to the formation of chlorine. A. Classen (*Zeit. anal. Chem.*, **17.** 182, 1878) says that ignited ferric oxide dissolves at once in concentrated hydrochloric acid if the powdered material be previously boiled to a flocculent condition with caustic potash solution. The alkaline liquid is decanted off and the acid added. T. M. Brown (*Iron*, 361, 1878; *Dingler's Journ.*, **228.** 378, 1878; E. Donath and R. Jeller, *Zeit. anal. Chem.*, **25.** 361, 1886) ignites the powdered material intimately mixed with from half to its own volume of powdered zinc. The mixture is ignited in a porcelain crucible for 5–8 minutes. The mass is transferred from the crucible to a flask, and dissolved in dilute sulphuric acid (1 : 2). Portions adhering to the crucible can be removed by washing with dilute acid. The zinc must be free from iron. The ferric oxide is reduced to metal. Chromium oxide and alumina are not reduced to metals by the ignition with zinc powder. H. von Jüptner (*Oester. Zeit. Berg. Hütt.*, **42.** 469, 1894) recommends magnesium powder in place of zinc. E. Hart (*Chem. News*, **34.** 65, 1876; J. S. Maclaurin and W. Donovan, *Journ. Soc. Chem. Ind.*, **28.** 827, 1909) reduces the ore in a stream of hydrogen gas for 10–30 minutes (page 269). The sample is then usually easily decomposed by hot dilute acid. F. Michel, *Chem. Ztg.*, **36.** 345, 1912.

[1] Potassium nitrate is generally recommended for this purpose. The nitrite neither froths nor attacks the crucible so much as the nitrate.

[2] G. W. Dean, *Journ. Amer. Chem. Soc.*, **28.** 882, 1906; **29.** 1208, 1907; T. G. Timby, *ib.*, **30.** 614, 1908; H. E. Ashley, *Chem. News*, **90.** 274, 1904.

[3] V. Macri, *Monit. Scient.* (4), **20.** 18, 1906; A. Kaysser, *Chem. Ztg.*, **35.** 94, 1911 (bog iron ores); F. Michel, *Chem. Ztg.*, **36.** 345, 1912.

The manganates, later on, oxidise the ferrous salts, leading to low results when the solution of the fused mass is titrated with permanganate.[1]

(2) Fusion with borax—Hermann's process. Here high results are obtained owing to the reduction of ferric salts during the fusion.[2]

(3) Digestion in a sealed glass tube with sulphuric acid, or a mixture of hydrofluoric[3] and sulphuric acids, at 150–200°. This method furnishes very fair results in the absence of sulphides.[4]

(4) Digestion in a platinum crucible with a mixture of hydrofluoric and sulphuric acids, in an atmosphere of carbon dioxide.[5]

The silicate, when decomposed by one of the methods—(4) for preference—indicated above, is titrated with a standard solution of potassium permanganate for the ferrous iron.[6]

Dissolution of the Ferrous Iron.—From 0·3 to 1 grm. of the sample, powdered as coarsely as will permit of its decomposition by the acids in a reasonable time,[7] is placed in a platinum crucible or dish—approximately 40–50 c.c.—and stirred up with 15 c.c. of dilute sulphuric acid (1 : 3).[8] The stirring must be thorough, since the powder may "cake" at the bottom of the dish and escape attack by the acids later on. Place the dish *A* on a support, fig. 152, in Treadwell's decomposition vessel,[9] which consists of a leaden box *B* supported in a paraffin[10] bath *C*. The leaden cover has two holes *D* and *E*. A rapid stream of carbon dioxide gas[1] is passed through *D* for about 5 minutes. The lead cover is removed, and about 10 c.c. of concentrated hydrofluoric acid[2] (40 per cent.) is added to the crucible. The dish is placed directly under the opening *E*. This permits the contents of the crucible to be stirred with a stout platinum wire. The bath is now heated to about 100°, and maintained at that temperature for about an hour. The aperture *T* allows a thermometer to be placed in the paraffin bath *C*. Some of the excess of hydrofluoric acid may be driven off by raising the temperature to 120° for another hour. It is important not to work too long at the higher temperature, for the reason indicated above. There should now be no grit representing undecomposed mineral in the crucible. The use of silicic acid later on renders a prolonged heating to drive off hydrofluoric acid unnecessary. Keep the stream of carbon dioxide flowing through the apparatus all the time. Let the system cool, while still maintaining the current of gas.

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[1] W. Early, *Chem. News*, **30**. 169, 1874.

[2] R. Hermann, *Journ. prakt. Chem.* (1), **15**. 105, 1838; W. Suida, *Tschermak's Mitt.* (1), **5**. 176, 1876; C. Bodewig, *Pogg. Ann.*, **158**. 222, 1876; C. Rammelsberg, *Zeit. deut. Geol. Ges.*, **24**. 69, 1872; H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**. 699, 1871.

[3] Presumably the hydrofluoric acid is not exhausted by attacking the glass before it has had time to affect the substance under investigation. According to W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, **422**. 158, 1910), the addition of hydrofluoric acid is "of doubtful utility."

[4] A. Mitscherlich, *Journ. prakt. Chem.* (1), **81**. 116, 1860; (1), **83**. 445, 1861; *Zeit. anal. Chem.*, **1**. 56, 1862; C. Doelter, *ib.*, **18**. 50, 1879; *Tschermak's Mitt.* (1), **7**. 281, 1877; (2), **3**. 100, 1880; A. Remelé, *Notizblatt*, **3**. 160, 1867: **4**. 173, 1868. W. Michaelis (*ib.*, **5**. 204, 1869) says all the clay is not decomposed. For hydrochloric acid in sealed tubes—A. H. Allen, *Chem. News*, **22**. 57, 1870; S. Piña de Rubies, *Anales Fis. Quim.*, **10**. 78, 1912. For operating with sealed tubes, consult page 493.

[5] G. Werther, *Journ. prakt. Chem.* (1), **91**. 321, 1864; J. P. Cooke, *Amer. J. Science* (2), **44**. 347, 1867; J. H. Pratt, *ib.* (3), **48**. 149, 1894; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 415, 1911; F. Mohr, *Zeit. anal. Chem.*, **7**. 450, 1867; A. R. Leeds, *ib.*, **16**. 323, 1877; C. E. Avery, *Chem. News*, **19**. 270, 1869. C. A. Wilbur and W. Whittlesey (*ib.*, **22**. 2, 1870) use a mixture of calcium fluoride and hydrochloric acid; and A. H. Chester and F. I. Cairns (*Amer. J. Science* (3), **34**. 113, 1883) use a mixture of ammonium fluoride and sulphuric acid.

[6] J. M. Eder (*Monats. Chem.*, **1**. 137, 140, 1880) suggests the following gravimetric process for the determination of ferrous oxide in the presence of organic matter and ferric oxide. The solution must not be too strongly acid:—Add an excess of neutral potassium oxalate and silver nitrate. In a few minutes add sufficient tartaric acid to prevent the precipitation of ferric hydroxide on addition of ammonia. Add an excess of ammonia. The addition of some ammonium chloride here favours the filtration and washing of the precipitate. The precipitated silver may be dissolved in nitric acid, precipitated, and weighed as silver chloride. From this, the ferrous oxide can be determined by computation from the equation: $2FeO + Ag_2O = Fe_2O_3 + 2Ag$. Hence, 1 grm. of silver represents 0·666 grm. FeO; or 1 grm. of silver chloride represents 0·5017 grm. FeO.

[7] Some silicates—particularly those poor in silica and rich in magnesia, are liable to "cake" on the bottom of the crucible and escape attack by the acid. M. Dittrich (*Ber.*, **44**. 990, 1911) recommends that the powdered mineral be intimately mixed with coarsely ground quartz, which resists attack by the hydrofluoric acid long enough for the mixed acids to attack the mineral. The quartz also exposes a larger surface of the mineral to the attack.

[8] If carbonates be present the mixture may effervesce. Hence, the acid must be added slowly to the dish and covered with a watch-glass to prevent loss by spurting. The cover must be afterwards rinsed into the dish. There is little danger of oxidation of the ferrous iron at this stage.

[9] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 416, 1911.

[10] Instead of paraffin, L. W. Bosart (*Journ. Amer. Chem. Soc.*, **31**. 724, 1909; *Chem. News*, **100**. 238, 1909) recommends a mixture of 10 parts refined cotton seed oil and 1 part of beeswax. It fumes but little below 250°, and its flash-point in an open cup is above 300°; hard

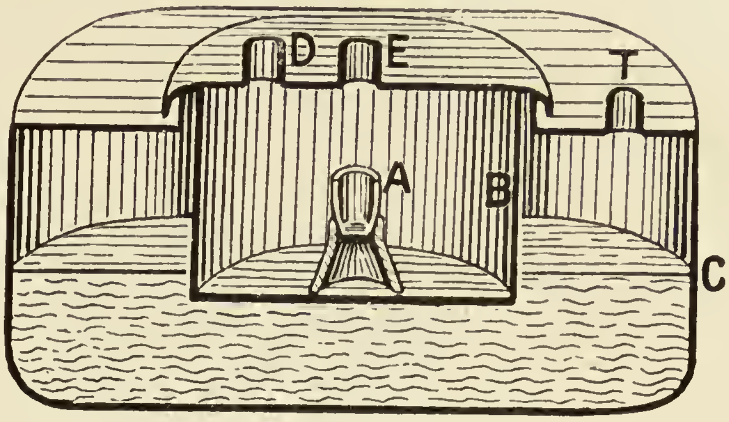

FIG. 152.—Treadwell's apparatus (section).

An alternative and simpler method of decomposing the mineral—not quite as effective—is as follows :—

Fit a 50-c.c. platinum crucible tightly into a hole in the centre of a piece of asbestos millboard so that the crucible passes about half way through, and the joint between the crucible and asbestos is nearly air-tight. Moisten half a gram of the coarsely powdered sample in the crucible with water. Put in a couple of coils of platinum wire to prevent bumping. Add a cold mixture of 10 c.c. of hydrofluoric acid and 15 c.c. of dilute sulphuric acid (1 : 3). Cover the crucible with a tight-fitting lid. Connect the top of a 15-cm. funnel[3] with a carbon dioxide generator. The funnel is placed over the crucible, and it should fit close to the asbestos millboard. When the air has been expelled by the carbon dioxide, place a Bunsen's burner below the crucible (fig. 153) so that the tip of the flame is about 3 inches below the bottom of the crucible, and the flame is raised or lowered so that the contents of the crucible boil gently. The motion prevents the particles of silicate from caking on the bottom. In 5 or 10 minutes the mineral will be decomposed. The burner is removed. When the steam in the crucible has condensed, the crucible is lifted with a pair of tongs (fig. 66),[4] without removing the lid, and plunged beneath the surface of 400–500 c.c. of cold, recently boiled distilled water contained in an 800-c.c. beaker. The lid of the crucible is removed and the contents are ready for titration.[5]

Titration for the Ferrous Oxide.—Thoroughly stir about 10 grms. of pure

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paraffin under same conditions flashed at 215°. Like paraffin, the mixture solidifies on cooling, but it melts more quickly than paraffin. Special oils, with a flash-point over 300°, are now sold for charging oil baths—H. Giesen, Duisburg-Wanheimerort.

[1] Purified as indicated on page 169.

[2] Hydrofluoric acid may contain reducing agents: arsenious acid, hydrogen sulphide, etc.—C. Jehn, *Zeit. anal. Chem.*, **13**. 176, 1874 ; *Archiv Pharm.* (3), **1**. 481, 1873. If the acid be made in leaden vessels it frequently contains sulphurous acid. If present, it must be destroyed by the addition of potassium permanganate until the colour just ceases to be discharged—W. Hampe, *Chem. Ztg.*, **15**. 1777, 1891. See pages 169 and 226.

[3] Coated inside with paraffin wax.

[4] A loop of platinum wire may be fixed round the crucible before it is placed on the asbestos millboard, for convenience in lifting and transferring the hot crucible to the beaker of water.

[5] A reddish-brown sediment which dissolves when stirred up with water is not to be mistaken for undecomposed mineral.

silicic acid [1] with about 100 c.c. of water in a 600-c.c. beaker, and add 20–25 grms. of potassium sulphate. Wash the hot contents of the platinum crucible into the beaker. Titrate as rapidly as possible with standard permanganate (page 198). The first permanent pink blush is the end point. This fades in a short time. It is well to confirm the method by a blank test, or with ferrous sulphate solution which has been standardised with hydrofluoric acid. One grm. of $KMnO_4$ represents 2·27412 grms. FeO. The amount of ferric oxide corresponding with the ferrous oxide so determined is calculated by multiplying the amount of ferrous oxide by 1·111343. Subtract the result from the total amount of ferric oxide determined in the sodium carbonate fusion as indicated on page 182.

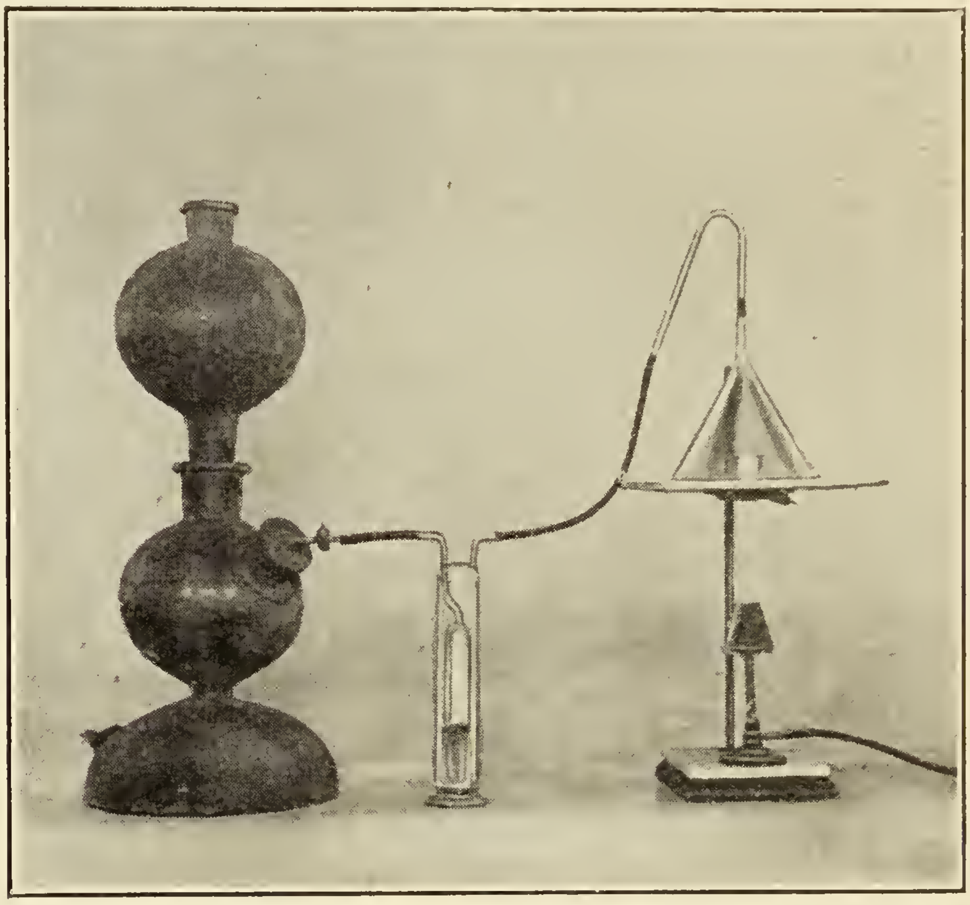

FIG. 153.—Opening silicates for the determination of ferrous iron.

EXAMPLE.—The sodium carbonate fusion, etc. (page 182), furnished 3·65 per cent. of Fe_2O_3. In the above determination, 1 grm. of the sample required 6·2 c.c. of permanganate containing 0·00098 grm. $KMnO_4$ per c.c. That is, 0·006076 grm. $KMnO_4$, *i.e.* 0·006076 × 2·274 grms. FeO. Hence, the substance has 0·0138 per cent. of FeO. But 0·0138 grm. FeO corresponds with $0·0138 \times 1·1113 = 0·0152$ grm. Fe_2O_3, that is, 1·52 per cent. Fe_2O_3. Hence, the sample has 3·65 less $1·52 = 2·13$ per cent. of ferric oxide —Fe_2O_3.

It is probable that the results for ferrous oxide are usually a little too low.

§ 242. Disturbing Factors in the Determination of Ferrous Oxide.

This subject has been carefully studied by Hillebrand and Stokes, and after a comparison of the different methods in use for the determination of ferrous oxide in silicates insoluble in the mineral acids, it has been stated that, "despite the utmost care in practical manipulation, the exact determination of ferrous iron in rocks is fraught with extraordinary difficulties and uncertainties. Only in the absence of decomposable sulphides and carbonaceous matter, and when the amount and condition of the vanadium are known and relatively coarse powders can be used, is it permissible to regard the result as fairly above suspicion."

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[1] Or enough to neutralise all the hydrofluoric acid which is present.

1. *The Influence of Fine Grinding.*—The unavoidable oxidation of ferrous compounds during grinding was discussed on page 124. "Nearly all mineral analyses which have been made in the past are affected by more or less serious errors due to the oxidation of the iron during grinding. The error is greater, the more finely the sample is powdered" (Hillebrand).

2. *The Influence of Sulphides.*—When sulphides decomposable by the acids are present, some hydrogen sulphide, and possibly also some sulphur dioxide, are formed.[1] These gases will reduce some of the ferric oxide to ferrous oxide, and consequently the decomposed silicate will contain more ferrous iron than the undecomposed silicate. This is more particularly noticed when the decomposition of the silicate is effected in sealed tubes. The difference is not very marked when but small quantities—2 per cent.—of ferrous iron are present, but the error may amount to nearly 20 per cent. when about 10 per cent. of ferrous iron is present. 0·01 per cent. of sulphur may cause the ferrous iron to appear 0·135 per cent. too high. The oxidation of the sulphides, and the consequent reduction of the ferric oxide, are greatly accelerated by the presence of ferric salts. The acid mixture will scarcely attack pyrite, but in the presence of ferric salts the action is relatively quick. The iron of the sulphide—say, pyrrhotite—may also appear in the final titration as ferrous iron.[2]

3. *The Influence of Organic Matter.*—Carbonaceous matters will reduce the sulphuric acid in the sealed tube; and, in general, organic matter will reduce the ferric oxide and render the determination of the ferrous iron in a mixture nugatory.[3]

4. *The Influence of Vanadium.*—If appreciable quantities of vanadium be present as, say, V_2O_3,[4] a correction must be made for the permanganate used in converting $V_2O_3 \rightarrow V_2O_5$ during the titration (page 200). Every gram of V_2O_3 found in the sample will be equivalent to 1·5757 grms. of FeO in the consumption of permanganate. If the vanadium occurs in the form of V_2O_5, no correction will be required.

EXAMPLE.—If a silicate contains 0·11 per cent. of V_2O_3, and the FeO, calculated from the permanganate titration, is 2·11 per cent., it follows that 0·11 × 1·5767 = 0·17 per cent. is not FeO. The FeO corrected for the vanadium will then be 2·11 less 0·17 = 1·94 per cent. FeO.

5. *Influence of Hydrofluoric Acid on the Permanganate Titration.*—A solution of ferrous sulphate in fairly concentrated sulphuric acid oxidises somewhat slowly; but if a little hydrofluoric acid be added to the solution, the rate of

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[1] E. A. Wulfing, *Ber.*, **32**. 2217, 1899; J. H. L. Vogt, *Zeit. prakt. Geol.*, **7**. 250, 1899; L. L. de Koninck, *Ann. Soc. Géol. Belgique*, **10**. 101, 1883; *Zeit. anorg. Chem.*, **26**. 123, 1901; W. F. Hillebrand and H. N. Stokes, *Journ. Amer. Chem. Soc.*, **22**. 625, 1900; H. N. Stokes, *Amer. J. Science* (4), **12**. 414, 1901. T. Scheerer (*Pogg. Ann.*, **124**. 98, 1850) compared the results obtained by the different methods. See also A. Leonhard, *Ueber die Bestimmung des Eisenoxyduls in Gesteinen*, Heidelberg, 1912.

[2] If the sulphides have been determined, this can sometimes be corrected accordingly.

[3] J. T. Hewitt and G. R. Mann (*Analyst*, **37**. 179, 1912) titrate solutions of ferric iron in presence of organic matter with standard thiosulphate solution, using ammonium thiocyanate as indicator and a small quantity of copper sulphate as catalyst. The titration is continued until the red colour of the ferric thiocyanate disappears. The end point is not sharp, and better results are obtained by adding a slight excess of the standard thiosulphate, and titrating back the excess with an iodine solution, using starch as indicator.

[4] C. Czudnowicz, *Pogg. Ann.*, **120**. 20, 1863; O. Lindemann, *Zeit. anal. Chem.*, **18**. 99, 1879; W. F. Hillebrand and F. L. Ransome, *Amer. J. Science* (4), **10**. 120, 1900.

oxidation is considerably increased. Hence it is very important to expose the solutions containing ferrous iron as little as possible to the air before titration.

This discussion all shows that the presence of the hydrofluoric acid interferes with the accuracy of the permanganate titration. In the presence of hydrofluoric acid, the permanganate is decolorised very quickly, so that the permanent pink blush normally obtained with permanganate titrations is very fugitive in the presence of hydrofluoric acid. It is therefore difficult to get a distinct end point. At the best, the pink blush lasts but a few seconds, and this is even more fugitive with increasing amounts of ferrous oxide, and of hydrofluoric acid. If the solution be boiled some time with the idea of driving off part of the hydrofluoric acid, part of the ferrous iron may be transformed to ferric iron by the oxidising action of the sulphuric acid as it becomes more and more concentrated. Gage[1] states that hydrofluoric acid does not interfere with the titration in the presence of calcium phosphate, but, according to Leonhard, the action is then so slow that the end-point is uncertain. Dittrich and Leonhard recommend the addition of 1 to 2 grms. of potassium or sodium sulphate (not ammonium sulphate) to the mixture to facilitate the recognition of the end point of the permanganate titration.[2] That being the case, it is advisable to spend less time in driving off the excess of hydrofluoric acid, and avoid getting low results arising from the oxidation of ferrous iron during the concentration of the solution. Fromme also avoids the danger of reoxidation during the removal of hydrofluoric acid by neutralising the hydrofluoric acid with pure silica. The resulting hydrofluosilicic acid enables the titration to be conducted more accurately than in the presence of hydrofluoric acid.

6. *Influence of Manganous Salts.*—The manganous salt formed by the reaction between the permanganate and the ferrous iron is itself readily oxidised by permanganate in the presence of hydrofluoric acid, so that a sharp end reaction is difficult to obtain if much hydrofluoric acid be present, or if much manganous sulphate be present. The latter will occur when much ferrous iron is under investigation, so that the pink tint of the permanganate persists longer when but little ferrous iron is in question than with larger amounts. The more hydrofluoric acid used, the greater the apparent amount of iron found.[3]

7. *Influence of Titanium.*—According to Dittrich and Leonhard, titanium sesquioxide, Ti_2O_3, in the presence of ferric salts produces disturbing effects on the permanganate titration, and titanium is nearly always present in the analysis of silicate rocks. These effects can be obviated by pouring the contents of the crucible containing the hydrofluoric acid, etc., into a 600-c.c. beaker containing 100 c.c. of water mixed with about 10 grms. of precipitated silica, and 20–25 grms. of potassium sulphate. The mixture is quickly titrated with $\frac{1}{20}$N-$KMnO_4$.

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[1] H. Fromme, *Tschermak's Mitt.*, **28.** 329, 1909 ; R. B. Gage, *Journ. Amer. Chem. Soc.*, **31.** 381, 1909 ; M. Dittrich and A. Leonhard, *Ber. Vers. Oberrhein. geol. Ver.*, **2.** 92, 1910 ; *Zeit. anorg. Chem.*, **74.** 21, 1912 ; O. Follenius, *Zeit. anal. Chem.*, **11.** 177, 1872 ; E. Rupp, *Ber.*, **38.** 164, 1905 ; A. Leonhard, *Ueber die Bestimmung des Eisenoxyduls in Gesteinen*, Heidelberg, 1912.

[2] E. Deussen (*Zeit. anorg. Chem.*, **44.** 425, 1905 ; *Monats. Chem.*, **28.** 163, 1907) recommends manganese sulphate ; but this is apparently a mistake—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422.** 162, 1910.

[3] F. J. Metzger and L. E. Marrs, *Journ. Ind. Eng. Chem.*, **3.** 333, 1911.

CHAPTER XXXIV.

THE DETERMINATION OF CHROMIUM, VANADIUM, AND URANIUM.

§ 243. The Errors due to the Presence of Chromium, Vanadium, and Uranium.

VANADIUM is a fairly common constituent of fireclays.[1] If chromium, vanadium, and uranium be present in a silicate, they will be precipitated with the aluminium, iron, and titanium.[2] Consequently, these elements will be found in the products of the pyrosulphate fusion, and, if ignored, they may introduce two errors in the analysis:

1. *The iron determination will be too high.* Vanadic acid—V_2O_5—is reduced by hydrogen sulphide to V_2O_4; by magnesium in sulphuric acid solution, and by ammonium bisulphite, to V_2O_3; and by metallic zinc, more or less completely to V_2O_2.[3] The colour of the solution undergoing reduction passes from yellowish (V_2O_5) to blue (V_2O_4), to green (V_2O_3), to lavender (V_2O_2). The reduced oxides —V_2O_4, V_2O_3, and V_2O_2—are converted to V_2O_5 by titration with permanganate. Consequently, the action of, say, one molecule of V_2O_3 on the potassium permanganate will be equivalent to the effect of two molecules of reduced ferric oxide; and the action of a molecule of V_2O_4, the same as one molecule of reduced ferric oxide. Hence, with the ammonium bisulphite reduction, every gram of vanadium pentoxide, V_2O_5, corresponds with 0·875 grm. of ferric oxide —Fe_2O_3—and with the magnesium reduction, to 1·751 grms. of ferric oxide.[4]

EXAMPLE.—A fireclay containing 0·09 per cent. of vanadium pentoxide showed 2·15 per cent. of ferric oxide by the ammonium bisulphite reduction and permanganate titration. Hence, the effect of the reduced vanadic oxide was the same as 0·09 × 0·8755 = 0·08 grm. Fe_2O_3. Hence, the clay had 2·15 less 0·08 = 2·07 per cent. of ferric oxide.

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[1] A. Terreil, *Compt. Rend.*, **51.** 94, 1860; see Vol. II.

[2] Note, if certain members of the hydrogen sulphide group be removed before the ammonia precipitation is made, some uranium may be precipitated in that group. The addition of an *excess* of hydrogen peroxide before ammonia will prevent vanadium precipitating with aluminium, etc.—W. W. Clark, *Met. Chem. Eng.*, **11.** 91, 1913.

[3] The statement by B. Glasmann (*Ber.*, **38.** 600, 604, 1905) that metallic zinc reduces V_2O_5 to V_2O_2, while metallic magnesium reduces V_2O_5 to V_2O_3, while both agents reduce molybdic acid to molybdenum sesquioxide, was also proposed as a volumetric process, with the permanganate titration, for the simultaneous determination of vanadium and molybdenum. F. A. Gooch and G. Edgar (*Amer. J. Science* (4), **25.** 233, 1908; *Chem. News*, **98.** 2, 1908), however, have shown that the action of magnesium is somewhat irregular. For a study of the conditions under which the sulphur dioxide reduction will reduce vanadium pentoxide to the tetroxide, and not attack molybdenum trioxide, see G. Edgar, *Amer. J. Science* (4), **25.** 332, 1908; *Chem. News*, **97.** 245, 1908. A solution containing vanadium dioxide cannot be exposed to the air momentarily without undergoing oxidation.

[4] Gooch and Newton's plan (page 189) for "the oxidation of Ti_2O_3 without the oxidation of ferric oxide does not work with V_2O_4, although it converts V_2O_3 to V_2O_4 if the solution be warm. This subject has not been properly investigated."—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422.** 109, 1910.

Chromic acid and the chromates are reduced by hydrogen sulphide, metallic zinc, magnesium, and aluminium in acid solution, sulphites, and stannous chloride. Uranium salts are also reduced by similar agents. The reduced salts are reoxidised by potassium permanganate. Hence, both chromium and uranium salts, in the pyrosulphate fusion, will introduce errors in the determination of iron by the titration process. If, therefore, appreciable quantities of these elements are present, other methods of separation must be employed, and an allowance made.

2. *The titanium determination will be too high.* Vanadium compounds give a reddish-brown—"brick-red"—coloration with hydrogen peroxide. This is a more intense coloration than the yellowish-orange tint due to titanium,[1] and, in consequence, vanadium may intensify the effect of titanium in Weller's colorimetric process, and thus lead to high results. With practice it is possible to tell if much vanadium is present from the tint obtained with hydrogen peroxide in Weller's process for titanium.[2]

§ 244. The Detection of Chromium and Vanadium.

Fuse, say, 5 grms. of the finely powdered silicate with 20 grms. of sodium carbonate[3] and 3–4 grms. of sodium nitrite—$NaNO_2$. Extract the cold cake with hot water, and add a little alcohol to reduce the sodium manganate. Filter the solution. The filtrate contains some alumina, silica, arsenic, phosphorus, fluorine, chlorine, sulphur, molybdenum, chromium, vanadium, tungsten, etc.; the residue may contain titanium, iron, uranium,[4] barium, zirconium, rare earths, etc. Nearly neutralise the filtrate with nitric acid, but keep the sodium carbonate in slight excess. Evaporate the solution to dryness, take up the mass with water, and filter. Add mercurous nitrate to the alkaline solution, when mercurous arsenate chromate, molybdate, and tungstate may be precipitated. Boil the solution and filter. Dry and ignite the precipitate in a platinum crucible, fuse with sodium carbonate, and extract the fused mass with water.

Chromium.—A yellow solution probably indicates chromium.[5] The tint of the solution deepens on the addition of, say, sulphuric acid. Pour a little of the solution into a test tube, add an excess of hydrogen peroxide, and shake up the mixture with 3 c.c. of ether. A blue coloration in the ethereal solution floating on the aqueous solution represents chromium.[1] See page 484.

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[1] An experienced eye can frequently recognise the presence of vanadium from the tint of the solution prepared for the colorimetric determination of titanium.

[2] According to H. J. H. Fenton (*Journ. Chem. Soc.*, **93**. 1064, 1908), a cold aqueous solution of dihydroxymaleic acid gives a straw-yellow coloration in the presence of 1 part of titanium (as titanic salt, say $TiCl_4$) in 1,000,000 parts of solution; a lemon-yellow with 1 : 150,000; and an intense orange-red with 1 : 15,000. The coloration is approximately "fifteen to twenty times as delicate as the hydrogen peroxide test," and "it is not given by vanadium." Molybdates and uranyl salts give red or brown colours which are destroyed by acids—the former by heating, the latter in the cold. Tungstic acid gives a brown coloration which immediately becomes blue. Negative results are obtained with salts of thorium, cerium, zirconium, silica, and tin. Ferric salts interfere by destroying the reagent. Ferrous salts do not interfere. Hence the reaction can be used for detecting titanium in presence of vanadium.

[3] H. L. Robinson (*Chem. News*, **70**. 199, 1894) reports the presence of vanadium in commercial sodium hydroxide.

[4] Treat the residue with nitric acid, and test by boiling the solution with an excess of sodium carbonate. It is perhaps advisable to indicate here a few of the *important reactions of uranium salts.* Potassium hydroxide with uranic salts precipitates a yellow potassium uranate, $UO_2.O(OK)_2$; ammonium hydroxide, a yellow ammonium uranate, $UO_2.O(ONH_4)_2$; sodium carbonate, a yellow uranyl sodium carbonate, $UO_2Na_4(CO_3)_3$. Ammonium sulphide precipitates a brown uranyl sulphide, UO_2S, which is soluble in ammonium carbonate and in dilute acids. Uranyl salts accordingly give no precipitate with ammonium sulphide in the presence of ammonium carbonate. Potassium ferrocyanide gives a brown precipitate of uranyl ferrocyanide, either $UO_2.K_2FeCy_6$ or $(UO_2)_2FeCy_6$. Sodium phosphate gives a yellowish-white uranyl phosphate, UO_2HPO_4, which passes into ammonium uranyl phosphate in the presence of ammonium salts.

[5] Note, zinc and chromates may form insoluble zinc chromate in alkaline solutions—G. Chancel, *Compt. Rend.*, **43**. 927, 1856.

Vanadium.—Acidify a portion of the solution with sulphuric acid, and precipitate molybdenum, if present, by hydrogen sulphide in a pressure flask (page 277). If tin be present, oxalic acid will keep it in solution. Molybdenum, arsenic, traces of platinum, etc., will be precipitated, if present. The filtrate from the precipitated sulphides is boiled while a current of carbon dioxide is passing through the solution in order to drive off the hydrogen sulphide. Evaporate the solution to dryness, and remove the excess of sulphuric acid in an air bath. Dissolve the residue in water, and add a few drops of hydrogen peroxide. A characteristic "brick-red" coloration develops if vanadium be present.[2]

§ 245. The Separation of Chromium, Iron, Titanium, Aluminium Vanadium, and Uranium from Manganese, Cobalt, Nickel, and Zinc.

Chromium in the Basic Acetate Separation.—In applying the basic acetate process, it may be remembered that both chromium acetate and chromium hydroxide are easily soluble in acetic acid. It might therefore be supposed that some of the chromium will be dissolved when the basic precipitation is made in the presence of free acetic acid. Some claim that practically all the chromium can be precipitated with the iron and aluminium, even in the presence of some free acetic acid, because the chromium acetate seems to assume a kind of "passive state" towards acetic acid, particularly when the chromium is in very large excess; but it is necessary to make sure the chromium has all been precipitated by adding hydrogen peroxide to the filtrate. A blue coloration shows that chromium is present in the filtrate.[3] Some recommend transforming the chromium salts into chromates before applying the basic acetate process. Most of the chromium then passes into the filtrate along with some of the aluminium as aluminium chromate, but a part remains with the precipitate in the form of basic chromates of iron and aluminium.[4]

The error due to the formation of basic ferric chromates is least when the precipitation of the iron from the chromate solution is made with sodium hydroxide in sufficient excess to decompose the basic ferric chromate. If but a small amount of iron be present, the excess need not be very large.[1] Sodium carbonate is quite as good provided also a sufficient excess be used. Thus Brearley[2] found that in a litre of solution containing the equivalent of 1 grm. of iron (and 0·5 grm. of aluminium), and 0·375 grm. of potassium chromate, the addition of a varying excess of alkali led to the results shown on the left of Table LX.; and with solutions containing half a gram per litre of aluminium in place of iron, a varying excess of alkali furnished the results shown on the right of the same table.

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[1] A. Terreil (*Bull. Soc. Chim.* (2), **3**. 30, 1865; *Chem. News*, **11**. 136, 1865) precipitates the chromium as lead chromate. This is all right if molybdenum, etc., are absent. W. Gibbs (*Amer. J. Science* (2), **39**. 59, 1865; (3), **5**. 110, 1873; *Chem. News*, **28**. 63, 1873) separates uranium from chromium quantitatively or qualitatively by precipitating the uranium with a slight excess of sodium hydroxide. The uranium will be found in the precipitate, the chromium in the filtrate. If a little chromium be present in the precipitate, it can be removed by dissolving the precipitate in dilute nitric acid, boiling to expel nitrous fumes, etc., as described below, and finally precipitating the chromium as mercurous or barium chromate.

[2] C. M. Johnson (*Rapid Methods for the Chemical Analysis of Special Steels*, New York, 5, 1909) states that ferrous ammonium sulphate will discharge the brick-red coloration of vanadium more quickly than the yellowish-orange tint of titanium compounds. Hence, if ferrous ammonium sulphate be added to a solution containing both vanadium and titanium in the presence of hydrogen peroxide, the brick-red colour will fade to a bright yellow tint before the colour is discharged; if titanium be absent, the brick-red coloration will fade to a colourless solution without showing the yellow tint. Fenton's reaction—page 468—gives better results in detecting titanium in the presence of vanadium.

[3] B. Reinitzer, *Monats. Chem.*, **3**. 249, 1882; *Chem. News*, **48**. 114, 1883; F. Mayer, *Ber.*, **22**. 2627, 1889. One writer says: "The method of separating ferric and aluminium salts in the form of basic acetates entirely loses its applicability in the presence of chromium salts."

[4] H. Brearley, *Chem. News*, **76**. 175, 1897; **77**. 49, 179, 1898.

Table LX.—Effect of an Excess of Alkali on the Separation of Iron, Aluminium, and Chromium.

Excess of alkali 2N-sol.	Percentage separation.			Excess of alkali 2N-sol.	Percentage separation.		
	Sodium carbonate.	Sodium hydroxide.	Ammonia.		Sodium bicarbonate.	Ammonium carbonate.	Ammonia.
0	54·6	69·3	24·8	10	94·0	81·3	89·0
10	90·4	100·0	70·4	20	95·0	93·6	90·5
20	97·5	99·8	77·0	30	99·0	94·4	93·1
30	98·7	100·0	83·6				
50	100·1	...	87·8				

The results show that sodium carbonates or sodium hydroxide give good separations if a sufficient excess be used. But when chromium is to be separated from aluminium, *a large excess of alkali inhibits the precipitation of aluminium hydroxide, and favours the precipitation of ferric hydroxide.*

Consequently, as indicated on page 362, avoid the basic acetate process for the separation of chromium from manganese, cobalt, nickel, zinc, and ferrous salts. In many cases, the chromium will be precipitated with the aluminium, iron, and titanium both in the "basic acetate" and in the "ammonia" processes.[3] It then remains to separate the chromium from the iron, aluminium, and titanium by some other process, say Knorre's method, or the mercurous nitrate process.

The Barium Carbonate Method.—This method originated with Fuchs and Rose,[4] and it is more satisfactory than the basic acetate process when chromium is present. The barium carbonate process depends upon the fact that ferric, aluminium, chromium, vanadium, titanium, and uranium hydroxides are precipitated from cold dilute solutions in a few hours by barium carbonate, while manganese, nickel, cobalt, zinc, and ferrous salts are not precipitated. The barium is subsequently removed from both the precipitate and filtrate.

Ferric salts, etc., are readily hydrolysed (pages 181 and 362) in aqueous solutions:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl.$$

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[1] Similar remarks apply to the separation of molybdenum by this process—F. Ibbotson and H. Brearley, *Chem. News*, **81**. 269, 1900; **79**. 3, 1899.

[2] H. Brearley, *Chem. News*, **76**. 175, 1897; **77**. 49, 131, 179, 216, 1898; W. Galbraith, *ib.*, **77**. 187, 1898.

[3] It must be borne in mind that aluminium hydroxide and chromium hydroxide are slightly soluble in ammonia, so that the filtrate from the ammonia precipitate must be boiled to recover the aluminium and chromium, as indicated on page 479.

[4] J. N. von Fuchs (*Schweigger's Journ.*, **62**. 184, 1831) also used calcium carbonate. H. Rose, *Pogg. Ann.*, **83**. 137, 1851; J. F. W. Herschel, *Ann. Chim. Phys.* (3), **49**. 306, 1837.

In the presence of barium carbonate, the free acid will be removed as fast as it is formed: $BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$; equilibrium is disturbed; and the hydrolysis is completed. The net result of the action is represented by the equation:

$$2FeCl_3 + 6H_2O + 3BaCO_3 = 3BaCl_2 + 2Fe(OH)_3 + 3H_2O + 3CO_2.$$

If the solution be heated, the salts of zinc, nickel, etc., may also be hydrolysed, and, in consequence, precipitated by the barium carbonate treatment. If much nickel and cobalt be present, small amounts of these elements will be precipitated by the barium carbonate even in the cold. The presence of ammonium chloride,[1] however—about 5 grms. per 100 c.c. of solution—prevents the precipitation of nickel and cobalt, and the results are then quite satisfactory. The method has also been recommended for separating vanadium and chromium from ferrous iron[2] and manganese. With these elements, the separation is effected after a few minutes' boiling with barium carbonate.[3] Zinc hydroxide[4] and cadmium carbonate[5] have also been proposed in place of barium carbonate. The cadmium can be removed by subsequent treatment with hydrogen sulphide. The *modus operandi* is as follows:—

The slightly acid solution containing nitrates or chlorides of the elements indicated above, but free from sulphates,[6] is treated in an Erlenmeyer's flask with a solution of sodium carbonate, as in the basic acetate process, until a slight permanent turbidity is produced. This is cleared by a drop or two of dilute hydrochloric acid. The dilute solution is thoroughly agitated with an emulsion of barium carbonate (that is, barium carbonate suspended in water).[7] The flask is closed and allowed to stand several hours, with occasional shaking. Decant the clear solution through a filter paper, and wash the residue three times with cold water; wash the precipitate on to the filter paper by means of cold water.

(*a*) *The precipitate* is dissolved in hydrochloric acid; heated to boiling to remove the carbon dioxide; and the iron, vanadium, chromium, aluminium, titanium, and uranium are either precipitated by ammonium sulphide, or the barium is removed by means of sulphuric acid or sodium sulphate. The latter process is not so good as the former, because the barium sulphate is liable to carry down some of the metals from the solution.

(*b*) *The filtrate* from the barium carbonate is heated to boiling and treated with sulphuric acid or sodium sulphate to precipitate the barium. The precipitate is washed. The filtrate contains manganese, cobalt, nickel, zinc, and ferrous salts,[8] if present.

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[1] P. Schwarzenberg, *Liebig's Ann.*, **97**. 216, 1856.

[2] It is almost impossible to prevent the precipitation of a little iron from "ferrous solutions," but the error from this effect is so small that C. R. Fresenius (*Quantitative Chemical Analysis*, London, **1**. 434, 1876) recommended the process in special cases for the separation of ferrous iron from ferric iron, etc.

[3] A. Steffan, *Ueber die Bestimmung von kleinen Mengen an Chrom und Vanadin in Gestein und Stahlarten*, Zürich, 1902.

[4] P. Slawik, *Chem. Ztg.*, **34**. 648, 1910.

[5] J. R. Cain, *Bull. Bur. Standards*, **7**. 377, 1911.

[6] The solution must be quite free from sulphates because the other elements may be precipitated, *e.g.*: $ZnSO_4 + BaCO_3 \rightleftharpoons ZnCO_3 + BaSO_4$.

[7] BARIUM CARBONATE.—The barium carbonate must be tested by dissolving a portion of it in hydrochloric acid and precipitating the barium by the addition of sulphuric acid; the filtrate must leave no residue when evaporated to dryness in a platinum dish, showing that the barium carbonate is free from alkaline carbonates, etc.

[8] As a rule, the ferrous iron is oxidised to the ferric state, so that no iron remains in the filtrate.

The main objection to the cold process—particularly with chromium—is the time required for the precipitation, and the subsequent removal of barium. The precipitation can, of course, be allowed to proceed overnight when the results are not urgently wanted. As indicated above, in the special case where chromium and vanadium have to be separated from manganese and ferrous salts, the solution can be heated to boiling, and small additions of barium carbonate made every two or three minutes until an excess of about 1 to 2 grms.[1] has been added. After 10 to 15 minutes' boiling, let the mixture stand a few minutes to allow the precipitate to settle, filter and wash the residue with hot water. Place the filter paper and precipitate in a large platinum crucible; burn off the filter paper; and fuse the residue with about 2 grms. of sodium carbonate and $\frac{1}{4}$ grm. of sodium nitrite. The fused mass is extracted with water; ferric oxide remains undissolved, while sodium aluminate, chromate, and vanadate pass into solution. The chromate is treated with acetic acid and lead acetate, or with dilute nitric acid and lead nitrate, for the precipitation of lead chromate and lead vanadate, as indicated below.

§ 246. The Separation of Chromium and Vanadium in the Analysis of Silicates.

Decomposition of the Silicate.[2]—Fuse 5 grms. of the powdered sample with about 20 grms. of sodium carbonate and 3 grms. of sodium nitrite. Extract with water; reduce the sodium manganate with a few drops of alcohol;[3] nearly neutralise the solution with nitric acid—about 150 c.c. of acid (sp. gr. 1·5) will be needed. The solution must not be acid or nitrous acid will be liberated, and this, in turn, will reduce some of the chromium and some of the vanadium.[4] Evaporate the solution to dryness; take up the mass with water; and filter. Ignite the precipitate; treat the ignited mass with sulphuric and hydrofluoric acids; evaporate to dryness; fuse with sodium carbonate; take up the mass with water; neutralise with nitric acid; boil; filter; and add the filtrate to the main solution. The object of this treatment is to recover chromium which is retained by the precipitated silica.

Precipitation of Chromium and Vanadium.—Add an almost neutral solution of mercurous nitrate[5] to the cold, barely alkaline solution until no further precipitation takes place. A bulky precipitate[1] containing mercurous carbonate, chromate, and vanadate is obtained.[2] Boil; filter; wash with water containing a little mercurous nitrate or ammonium nitrate in solution; dry the precipitate; and transfer as much as possible to a platinum crucible. Burn the filter paper separately, and add the ash to the main precipitate, which is ignited to remove the mercury. Fuse the residue with sodium carbonate, leach with water, and filter the yellow solution of sodium chromate into a small flask—25–50 c.c. If chromium *alone* be present, and the amount small, it is determined colorimetrically; if the amount be relatively large, it is determined volumetrically or gravimetrically. If *both* chromium and vanadium be present, they can be determined as described below, § 247 and § 252; or § 253.

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[1] Too much barium carbonate makes the subsequent extraction of the chromium difficult.

[2] W. F. Hillebrand, *Amer. J. Science* (3), **6**. 210, 1893; *Chem. News*, **78**. 216, 1893. The higher oxidation products—chromates—are not precipitated by ammonia. Hence, the silicate can be decomposed with the sodium peroxide fusion in a nickel crucible and the cake taken up with hydrochloric acid. The silica is removed as usual. The alumina is precipitated by boiling the solution made alkaline with ammonia and hydrogen peroxide. The precipitate is washed with a solution of ammonium nitrate, redissolved, and reprecipitated with ammonia and hydrogen peroxide as before. The alumina is then practically free from vanadium. The vanadium and chromium remain in the filtrate—W. Trautmann, *Stahl Eisen*, **30**. 1802, 1910.

[3] E. Classen (*Amer. Chem. Journ.*, 8. 437, 1896) shows that the undecomposed residue with some minerals requires re-fusion, since, if considerable vanadium be present and the vanadium is to be determined, the insoluble residue will always contain vanadium.

[4] If an excess of acid be added inadvertently, add a slight excess of sodium carbonate. The amount of acid required to neutralise 20 grms. of sodium carbonate can be determined by a blank test.

[5] Page 408. For the precipitation of vanadium as mercury vanadate, see C. R. von Hauer, *Journ. prakt. Chem.*, **69**. 385, 1856; C. Rammelsberg, *Ber.*, **1**. 158, 1868; E. Classen, *Amer. Chem. Journ.*, **7**. 349, 1885; C. Radau, *Liebig's Ann.*, **251**. 114, 1889; R. Holverscheit, *Ueber die quantitative Bestimmung des Vanadins und die Trennung der Vanadinsäure von Phosphorsäure*, Berlin, 10, 1890. It was formerly the custom to add a slight excess of mercurous nitrate and then mercuric oxide to neutralise the excess of nitric acid which is present in the solution of mercurous nitrate; but W. F. Hillebrand (*l.c.*) has shown that the mercuric oxide is not necessary, since the basic mercurous carbonate is sufficient to remove the small quantity of free nitric acid introduced along with the mercurous nitrate. Chlorides should be absent, or vanadium may be lost during the subsequent ignition of the precipitate.—E. B. Auerbach and K. Lange, *Zeit. angew. Chem.*, **25**. 2522, 1912.

Knorre's Process[3] *for separating Chromium.*—Dissolve the "ammonia" precipitate in dilute sulphuric acid, and add an excess of ammonium persulphate, with sufficient sulphuric acid to prevent the precipitation of basic ferric sulphate. On boiling, the dilute solution is converted into chromic acid. The iron and aluminium are then precipitated by ammonia in the usual manner. The precipitate is dissolved in dilute sulphuric acid, and the operation is repeated so as to eliminate the trace of chromium precipitated with the aluminium and iron.[4] The chromium is determined in the joint filtrate in the usual manner by gravimetric or volumetric processes—§§ 249, 250, and 251, pages 476 to 479; and the precipitate, containing the aluminium, titanium, and iron, is treated as indicated on page 210.

§ 247. The Colorimetric Determination of Chromium.

A solution of an alkaline chromate is yellow. The intensity of the colour is proportional to the amount of chromate in solution.[5] If a solution (standard solution) containing a known amount of chromate has the same tint as another solution of equal depth of liquid (test solution), it is assumed that both solutions have the same amount of the alkaline chromate in solution.

Standard Solution of Potassium Chromate.—This is prepared by dissolving 0·5105 grm. of potassium chromate in a litre of water made alkaline with sodium carbonate. One cubic centimetre of this solution represents 0·002 grm. of Cr_2O_3. Pipette, say, 10 c.c. into the right test glass of the colorimeter.

Test Solution.—This is prepared by concentrating the solution under investigation and making it up to a definite volume—25, 50, or 100 c.c.—such that its colour is weaker than the standard solution. Pour this solution into the left test glass of the colorimeter.

Comparison.—Dilute the standard solution with water from a burette until its tint is the same as the test solution. If the tint of the test solution be faint,

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[1] If the precipitate is inconveniently large, cautiously add a little nitric acid and then a drop of mercurous nitrate to make sure that precipitation is complete.

[2] Tungsten, molybdenum, phosphorus, and arsenic, if present, will be precipitated.

[3] G. von Knorre, *Zeit. angew. Chem.*, **16**. 1097, 1903.

[4] R. B. Riggs (*Amer. J. Science* (3), **48**. 409, 1894; *Chem. News*, **70**. 311, 1894; W. J. Sell, *ib.*, **54**. 299, 1886; *Journ. Chem. Soc.*, **35**. 292, 1879) digests the precipitate in 100 c.c. of water, 10 c.c. of hydrogen peroxide, and 1 grm. of sodium or potassium hydroxide. When effervescence has ceased, separate the ferric hydroxide by filtration. The filtrate contains aluminium, and chromium (as chromate). Acidify with acetic acid, precipitate the aluminium with ammonia; and the chromium is determined in the filtrate either by the volumetric or gravimetric process. J. Clarke (*Journ. Chem. Soc.*, **63**. 1082, 1893) added sodium peroxide until the solution was alkaline, and instead of using hydrogen peroxide and sodium hydroxide—T. Poleck, *Chem. News*, **69**. 285, 1894; O. Kassner, *Archiv Pharm.*, **232**. 226, 1895; M. E. Pozzi-Escot, *Bull. Soc. Chim.* (4), **5**. 558, 1909.

[5] L. L. de Koninck, *Pharm. Ztg.*, **78**. 594, 1889; F. W. Richardson, W. Mann, and W. Hanson, *Journ. Soc. Chem. Ind.*, **22**. 614, 1903; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **176**. 80, 1900; F. L. Langmuir, *Ueber die quantitative Bestimmung des Chroms auf gewichtsanalytischen auf kolorimetrischen Wege*, Freiburg i. Br., 1906.

Nessler's tubes may be used and the solution examined through a vertical column instead of horizontally as in the titanium determination.

EXAMPLE.—250 c.c. of a solution (from, say, 1 grm. sample) were treated as indicated above. 48 c.c. of water were required to make 10 c.c. of a solution containing, say, 10 c.c. of the standard per 100 c.c. of solution (that is, 0·0002 grm. of Cr_2O_3 per c.c.) the same tint. Hence, $48 + 10 = 58$ c.c. of the standard solution were equivalent to the solution from the given sample. Consequently, the 250 c.c. (1 grm. of clay) had:

$$\frac{250 \times 0{\cdot}0002}{58} = 0{\cdot}00086 \text{ grm. of } Cr_2O_3,$$

that is, the sample has the equivalent of 0·086 per cent. of chromic oxide. The amount of chromic oxide can be deducted from the ammonia precipitate.

According to Horn,[1] the tint is most sensitive when about 0·00002 grm. of potassium chromate is present per 100 c.c. of solution.[2] The smallest amount of chromium which can be detected in distilled water is 0·000013 grm. per 100 c.c., but if the solution contains much less than about 0·004 grm. of chromic oxide, Cr_2O_3, per 100 c.c. the comparison is not satisfactory, and a greater quantity of the original sample must be taken.

Errors.—The following numbers represent the results which can be obtained with known mixtures:

Cr_2O_3 used	8·88	8·88	8·88	8·88	11·67	6·34	mgrms.
Cr_2O_3 found	8·45	9·01	8·91	9·29	11·54	6·27	mgrms.
Error	−0·43	+0·13	+0·03	+0·41	− 0·13	−0·07	mgrm.

If vanadium be present, the solution can be reserved for the determination of vanadium by the volumetric process; if manganese be present, see page 384.

§ 248. The Analysis of Chromites and Chromic Oxides.

In the analysis of chromite (chrome iron ore), and also of the ignited chromic oxides used as colouring agents, we have a special difficulty arising from the insolubility, or rather the extremely slow rate of solution, of the materials in acids. We therefore depend upon a preliminary fusion of the material with a suitable flux. Here again the action of the flux is so slow that it is important to grind the materials under investigation to a very fine powder, and to heat the mixture for a comparatively long time. There is a wide choice in the selection of the flux.[3] Sodium peroxide is now in almost general use. Here, the action is quick, and the extreme care in grinding is not so very important as with less active fluxes. The fusion with sodium peroxide, or with a mixture of potassium hydroxide and sodium peroxide, can be made in a nickel, iron,[1] copper, or silver[2] crucible. Platinum crucibles should not be used with caustic alkalies. If iron and chromium are alone to be determined, a porcelain crucible may be used. The procedure is as follows:—

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[1] D. W. Horn, *Amer. Chem. Journ.*, **35**. 253, 1906; M. Dittrich, *Zeit. anorg. Chem.*, **80**. 171, 1913.

[2] For a colorimetric reaction based upon the colour produced by mixing diphenylcarbazide and chromic acid, see P. Cazeneuve, *Zeit. angew. Chem.*, **13**. 958, 1900; *Bull. Soc. Chim.*, (3), **25**. 758, 1901; A. Moulin, *ib.* (3), **31**. 295, 1904; *Chem. News*, **89**. 268, 1904; F. L. Langmuir, *l.c.* See page 454.

[3] FLUXES FOR OPENING CHROMITE.—Numerous fluxes have been used for the chromite fusion (S. Rideal and S. Roseblum, *Chem. News*, **73**. 1, 1896; A. Müller, *Bull. Soc. Chim.* (4), **5**. 1133, 1909). For example: SODIUM HYDROXIDE ALONE (L. Duparc, *Ann. Chim. Anal.*, **9**. 201, 1904; L. Duparc and A. Leuba, *Ann. Chim. Anal. Chim.*, **9**. 201, 1908; H. N. Morse and W. C. Day, *Amer. Chem. Journ.*, **3**. 163, 1881; *Chem. News*, **44**. 43, 1881); POTASSIUM HYDROXIDE AND CHLORATE (H. Schwarz, *Liebig's Ann.*, **69**. 212, 1849; *Zeit. anal. Chem.*, **22**. 83, 530, 1883; H. Pellet, *Berg. Hütt. Ztg.*, **40**. 224, 1881); MAGNESIA OR LIME WITH CAUSTIC SODA (J. Clark, *Journ. Soc. Chem. Ind.*, **11**. 501, 1893; *Chem. News*, **24**. 286, 304, 1871; A. Christomanos, *Ber.*, **10**. 16, 364, 1877; *Zeit. anal. Chem.*, **17**. 244, 1878; P. Vekšin, *Berg. Journ.*, **4**. 437, 1908; J. Clouet, *Dingler's Journ.*, **193**. 33, 1869; *Zeit. anal. Chem.*, **17**. 244, 1878). *Clark's flux* is 1 part of the sample with 8 parts of a mixture of 5 parts of sodium hydroxide and 3 of calcined magnesia. Heat in a Bunsen's flame in a platinum crucible for about 40 minutes; WITH CALCIUM CHLORIDE (J. Massignon, *Journ. Anal. App. Chem.*, **5**. 465, 1891; J. Massignon and E. Watel, *Bull. Soc. Chim.* (3), **5**. 371, 1891); WITH SODIUM CARBONATE, (R. Kayser, *Zeit. anal. Chem.*, **15**. 187, 1876); WITH A MIXTURE OF SODIUM AND POTASSIUM CARBONATES (J. E. Stead, *Journ. I. S. Inst.*, i. 160, 1893). Stead's mixture is sometimes called

Sodium Peroxide Fusion.—Grind the substance to a fine impalpable powder

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the *tribasic flux*: 4 parts lime, 1 sodium carbonate, 1 potassium carbonate. It resembles *Kayser's flux*—2 parts of sodium carbonate, and 3 parts of lime; WITH BORAX (R. Fieber, *Chem. Ztg.*, **24**. 333, 1900; R. W. E. MacIvor, *Chem. News*, **82**. 97, 1900). SODA LIME AND SODIUM NITRATE (F. Calvert, *Dingler's Journ.*, **125**. 466, 1852; J. Fels, *ib.*, **224**. 86, 1877); WITH POTASSIUM CHLORATE (E. Reinhardt, *Zeit. anal. Chem.*, **13**. 430, 1889; J. B. Britton, *Chem. News*, **21**. 266, 1870; *Zeit. anal. Chem.*, **9**. 487, 1870; J. Fels, *ib.*, **18**. 498, 1879); AND BORAX GLASS (L. Perl and V. Stefko, *Stahl Eisen*, **24**. 1373, 1904). SODIUM PEROXIDE (W. Hempel, *Zeit. anorg. Chem.*, **3**. 193, 1893; H. K. Tompkins, *Chem. News*, **68**. 136, 1893; J. Clark, *Journ. Chem. Soc.*, **63**. 1079, 1893; E. H. Saniter, *Journ. I. S. Inst.*, **43**. 153, 1895; *Journ. Soc. Chem. Ind.*, **15**. 156, 1896; S. Ridcal and S. Roseblum, *ib.*, **14**. 1017, 1895; C. Glaser, *Journ. Amer. Chem. Soc.*, **20**. 130, 1898; *Chem. News*, **77**. 123, 1898; G. Tate, *ib.*, **80**. 235, 1899; H. Fresenius and H. Bayerlein, *Zeit. anal. Chem.*, **37**. 31, 1898—silver crucible); WITH SODIUM CARBONATE (L. Luechese, *Ann. Chim. Anal. App.*, **9**. 450, 1908; M. Höhnel, *Archiv Pharm.*, **232**. 222, 1886; C. Glaser, *Chem. Ztg.*, **18**. 1448, 1894); WITH SODIUM NITRATE AND SODIUM CARBONATE (J. A. Müller, *Bull. Soc. Chim.* (4), **5**. 1133, 1909); WITH SODIUM HYDROXIDE (J. Spuller and S. Kalman, *Chem. Ztg.*, **17**. 880, 1207, 1412, 1893). POTASSIUM PEROXIDE AND SODIUM CARBONATE (J. A. Müller, *Bull. Soc. Chim.* (4), **5**. 1133, 1909), BARIUM PEROXIDE (E. Donath, *Dingler's Journ.*, **263**. 245, 1887); WITH SODIUM CARBONATE (L. P. Kennicut and G. W. Patterson, *Journ. anal. Chem.*, **3**. 131, 1889). POTASSIUM CARBONATE WITH SODIUM HYDROXIDE (C. Hausermann, *Chem. Ztg.*, **15**. 1601, 1891); WITH SODIUM CARBONATE AND BORAX (W. Dittmar, *Exercises in Quantitative Analysis*, Glasgow, 128, 1887; *Dingler's Journ.*, **221**. 450, 1878; P. Hart, *Journ. prakt. Chem.* (1), **67**. 320, 1856; E. Waller and H. T. Vulte, *Chem. News*, **66**. 17, 1892; O. Nydegger, *Zeit. angew. Chem.*, **24**. 1163, 1911). SODIUM CARBONATE AND POTASSIUM CHLORATE (R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **29**. 29, 1890). AMMONIUM NITRATE AND CAUSTIC SODA (C. A. Burghardt, *Chem. News*, **61**. 260, 1890). POTASSIUM BISULPHATE (E. Clark, *Journ. Amer. Chem. Soc.*, **17**. 327, 1895; H. Tamm, *Chem. News*, **24**. 307, 1871; C. L. Oudesluys, *ib.*, **5**. 255, 1862; C. O'Neill, *ib.*, **5**. 199, 1862; F. A. Genth, *ib.*, **6**. 30, 1862; *Zeit. anal. Chem.*, **1**. 498, 1862; R. Namais, *Stahl Eisen*, **10**. 977, 1890; T. S. Hunt, C. O'Neill, and F. A. Genth, *Amer. J. Science* (3), **5**. 418, 1873), 1 part sample with 15 parts of potassium bisulphate; WITH SODIUM FLUORIDE OR CRYOLITE (H. Hager, *Untersuchungen*, Leipzig, **1**. 263, 1888; P. C. Dubois, *Zeit. anal. Chem.*, **3**. 401, 1864; S. Kern, *Chem. News*, **35**. 107, 1877; F. W. Clarke, *ib.*, **17**. 232, 1868; *Amer. J. Science* (2), **45**. 173, 1868); AND SODIUM NITRATE (H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 376, 1851). POTASSIUM HYDROXIDE AND THE ELECTRIC CURRENT (E. F. Smith, *Ber.*, **24**. 2182, 1891). HYDROCHLORIC ACID UNDER PRESSURE (P. Jannasch and H. Vogtherr, *Ber.*, **24**. 3206, 1891). HEATING IN CURRENT OF CHLORINE, etc. (R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **29**. 28, 1890). HEATING WITH BROMINE WATER IN SEALED TUBES some days (E. F. Smith, *Amer. J. Science* (3), **15**. 198, 1877); WITH SULPHURIC ACID (A. Mitscherlich, *Zeit. anal. Chem.*, **1**. 54, 1861; F. C. Philips, *ib.*, **12**. 189, 1873); J. Jones, *Chem. News*, **65**. 8, 1892). TREATMENT WITH A MIXTURE OF POTASSIUM CHLORATE AND NITRIC OR SULPHURIC ACID. This is not particularly suited for chromites, but it is satisfactory for some chromic oxides (F. H. Storer, *Proc. Amer. Acad.*, **4**. 352, 1869; *Chem. News*, **21**. 195, 1870; C. Brunner, *ib.*, **4**. 57, 1861).

[1] H. N. Morse and W. C. Day, *Amer. Chem. Journ.*, **3**. 163, 1881.

[2] All these crucibles are attacked. Porcelain may last from two to four times before it is cut through by the flux. Silver crucibles lose about half a gram per fusion. There is a danger in the use of silver crucibles from the fact that the crucible can be melted if heated at too high a temperature on the Bunsen's flame. Silver, copper, and lead may be found in the fusion after using a silver crucible—W. Dittmar, *Chem. Ztg.*, **15**. 1521, 1580, 1891. W. Bettel (*Chem. News*, **43**. 94, 1881) recommended a platinum crucible gilded inside for fusions with alkalies. See also J. L. Smith, *Chem. News*, **31**. 55, 1875. Gold crucibles would be cheaper, in view of the higher price of platinum. Nickel crucibles are generally used. They lose about 0·1 grm. per fusion under the conditions described in the text. One crucible is said to last 15–25 fusions after a little practice in their use—but this estimate is rather high. Gold is not attacked *chemically* by fused potassium hydroxide, but nickel forms nickel hydroxide—M. le Blanc and O. Weyl, *Ber.*, **45**. 2300, 1912. Some use copper crucibles. The contamination from copper crucibles is said to give least trouble in many complex analyses.

in an agate mortar, and, by means of a platinum spatula, intimately mix 0·5 grm. of the dry (110°) powder with about 8 grms. of sodium peroxide[1] in, say, a nickel crucible of not less than 50 c.c. capacity, and fitted as described on page 266. Heat the crucible gently over the tip of a Bunsen flame until the contents of the crucible are fluid—this takes about 10 minutes. Raise the temperature to low redness—say another 10 minutes. Cool. Place the crucible in a beaker (400 c.c.), cover the crucible with a watch-glass, and gradually add about 50 c.c. of cold water in such a way that the first addition of water flows slowly between the watch-glass and the crucible. The mixture bubbles up and dissolves in a few minutes.[2] Remove the crucible and rinse it carefully with water. Boil the solution about 10 minutes to decompose the sodium peroxide.[3] The oxides of iron, manganese, cobalt, and nickel (mainly from the crucible) remain as insoluble precipitates. The chromium, aluminium, and most of the silica, with a little magnesia and lime, remain in solution.

The solution is now so strongly alkaline that it would destroy the filter paper, if an attempt at filtration be made. Hence, add about 8 grms. of ammonium carbonate, so as to neutralise the greater part of the sodium hydroxide but still leave the latter in slight excess. Filter the solution into a litre flask, and wash the residue on the filter paper with water. See note, page 494.

§ 249. The Volumetric Determination of Chromium.

Make the solution up to the litre mark with water and determine the chromium in an aliquot portion.[4] Hence, pipette a portion from the litre flask; acidify the solution with a large excess of dilute sulphuric acid (1 : 4); and dilute to about 500 c.c. with cold water. Place some solid sulphate in a weighing bottle. Weigh. Add the solid salt in small portions at a time until the yellow colour of the chromate has disappeared, and a blue coloration is obtained when a drop is touched on a spot of potassium ferricyanide solution. The chromate is reduced and the ferrous sulphate is oxidised. Weigh the bottle again. The loss represents the amount of ferrous ammonium sulphate added to the solution. The action is usually represented :

$$2K_2CrO_4 + 6FeSO_4.(NH_4)_2SO_4.6H_2O + 8H_2SO_4 = Cr_2(SO_4)_3 + \text{etc.}$$

Titrate the solution with standard potassium permanganate solution. Then dissolve, say, 1·5 grms. of the ferrous ammonium sulphate in 500 c.c. of water acidulated with sulphuric acid (10 c.c. concentrated acid). Also make a blank experiment with acidulated water—500 c.c. We have now sufficient data to calculate the amount of chromium as chromic acid in the aliquot portion taken from the litre flask. Every gram of ferrous ammonium sulphate oxidised represents 0·06447 grm. of chromic oxide—Cr_2O_3; or 0·0853 grm. of chromic trioxide—CrO_3.[1]

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[1] Reject the crust, if any, formed at the top of the peroxide bottle. This is mainly carbonate and oxide. L. Archbutt (*Analyst*, 20. 3, 1895) reports a sample of sodium peroxide with 0·5 per cent. of alumina and ferric oxide.

[2] Sometimes it requires warming a little. If the residue be insoluble in dilute sulphuric acid (1 : 4), this means that some of the substance has not been decomposed. In that case, the portion not dissolved must be re-fused with the flux. If nitric acid be used to take up the cake, some chromate may be reduced by the acid. A. Leuba, *Ann. Chim. Anal. App.*, 9. 303, 1908. Note the formation of volatile chromyl chloride when sulphuric acid is heated with a chloride and a chromate.

[3] To ensure the decomposition of the peroxide, some here recommend an evaporation to dryness. Peroxides must be absent in order to prevent reducing the chromates to chromic oxide—Cr_2O_3—when the solution is acidified. If the solution is purple-coloured, add a gram of sodium peroxide, and boil another 10 minutes.

[4] H. Schwarz, *Zeit. anal. Chem.*, 22. 530, 1883 ; H. Bollenbach, *Chem. Ztg.*, 31. 760, 1907 ; H. Vignal, *Bull. Soc. Chim.* (2), 45. 171, 1886 ; *Chem. News*, 33. 195, 1886 ; T. W. Hogg, *Journ. Soc. Chem. Ind.*, 10. 340, 1891 ; R. L Leffler, *Chem. News*, 77. 156, 1898 ; W. Galbraith, *ib.*, 35. 151, 1877 ; 77. 187, 1898.

Error due to the Filtration of Chromate Solutions through Filter Paper.[2]—If chromic acid solutions be filtered through paper, low results may be obtained owing to a partial reduction of the chromate. This error can be avoided by filtering the solution through asbestos, or by oxidising the solution *after* the filtration. The effect is produced by both acid and alkaline solutions; it is more marked with hot than with cold solutions; and also more marked with the lower-grade papers. For instance, 200 c.c. of a solution containing the equivalent of 25 c.c. of potassium bichromate (1 c.c. = 0·01 grm. Fe) were digested for half an hour with a 12·5-cm. filter paper. In one case 50 c.c. of N-NaOH were added to the solution, and in another case 50 c.c. of N-H_2SO_4. The results are shown in Table LXI.

Table LXI.—Effect of Filter Paper on Chromate Solutions.

Filter paper.	Ash of filter paper.	Equivalent in c.c. $K_2Cr_2O_7$ remaining.			
		Hot (100°).		Cold.	
		Acid.	Alkaline.	Acid.	Alkaline.
Munktell's Swedish	0·0005	24·6	24·9	...	...
Schleicher and Schülls' 589	0·0003	23·8	24·2	25·0	25·0
Ordinary English	0·0028	23·6	24·6	25·0	25·0
French grey	0·0139	22·5	24·0	24·0	24·7

The error with the ordinary filtration of chromate solutions may be equivalent to just over 0·1 per cent. of chromium.

The residue on the filter paper can be dissolved in dilute sulphuric acid (1 : 4)[3] and the iron determined by titration (page 198). The result is usually calculated to FeO. The silica can be determined by evaporating the sodium peroxide fusion with hydrochloric acid, as described on page 167. An aliquot part of the filtrate is treated with ammonia for alumina as indicated under clay analysis. An aliquot portion of the solution from the silica filtrate is used for the determination of sulphur. Magnesia, manganese, and lime can be determined by the methods of pages 213, 218, and 374.

§ 250. The Gravimetric Determination of Chromium as Barium Chromate.

The Solubility of Barium Chromate.—This process[4] is based on the sparing solubility of barium chromate in water. One part of the salt dissolves in 87,000 parts of cold, and in 23,000 parts of boiling water.[5] The presence of acetic acid increases the solubility of the chromate; thus, 1 part of the salt dissolves in 3670 parts of water containing 1 per cent. of acetic acid. The presence of ammonium salts also makes the salt more soluble. For instance, 1 part of barium chromate dissolves in about 23,000 parts of water containing 0·5 per cent. of ammonium chloride; in 45,000 parts of water containing 0·5 per cent. of ammonium nitrate; in 50,000 parts of water containing 0·75 per cent. of ammonium acetate; and in

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[1] This process can also be used for evaluating alkaline chromates and bichromates.

[2] H. Jervis, *Chem. News*, **77**. 133, 1898; A. Allison, *ib.*, **96**. 1, 1907.

[3] If any remain undissolved, the original fusion was not complete.

[4] W. Gibbs, *Zeit. anal. Chem.*, **12**. 309, 1893; G. Chancel, *Compt. Rend.* **43**. 927, 1856.

[5] R. Fresenius, *Zeit. anal. Chem.*, **29**. 414, 1890.

24,000 parts of a 1·5 per cent. solution of ammonium acetate. Hence the solution in which the precipitation is made must be but faintly acid with acetic acid. Mineral acids should be absent, or, if present, approximately neutralised by the addition of sodium carbonate, followed by sodium acetate.[1]

Oxidation to Chromic Acid.—If the chromium be present in the lower state of oxidation, it must be converted into chromic acid by the addition of an oxidising agent. For example, warm the alkaline solution with potassium persulphate, or sodium peroxide, or hydrogen peroxide,[2] or bromine,[3] or chlorine.[4] Nitric acid is rather slow in action.[5] Potassium chlorate acts fairly well in the presence of hydrochloric acid, but there is a difficulty in removing the last traces of chlorine oxides, especially in dilute solutions.[6] If the chromium be already present in the form of chromate, there is no need for the oxidation.

Precipitation of Barium Chromate.—Neutralise the solution with acetic acid.[7] Add a hot solution of barium acetate,[8] slowly, drop by drop,[9] to the hot neutral or weakly acidified solution. Let the mixture stand until cold; and, when the precipitate has settled, wash five times by decantation with hot water.[10] Filter[11] through asbestos felt in a Gooch's crucible.[12] Wash the precipitate with dilute alcohol (alcohol 1 vol., water 10 vols.), and dry it in an air bath at 110°.[13]

The Ignition.—Heat the covered crucible in a saucer, gently at first, and finally over the full flame of a Teclu's burner. In about 5 minutes, remove the lid, and heat the crucible until the precipitate has a uniform yellow colour.[14] Cool the crucible in a desiccator, and weigh as barium chromate—$BaCrO_4$. Multiply the weight by 0·3 or by 0·2999 to get the equivalent amount of chromic oxide—Cr_2O_3.

Results.—Working with solutions containing the equivalent of 0·6886 grm. of $BaCrO_4$, the following numbers were obtained:

$BaCrO_4$ . . .	0·6922	0·6918	0·6876	0·6861	grm.
Error	+0·0036	+0·0032	−0·0010	−0·0025	grm.

The precipitate may be dissolved in hydrochloric acid, mixed with a solution of potassium iodide, and the liberated iodine titrated with sodium thiosulphate as indicated on page 352 for copper, etc.[15] Instead of barium acetate, lead nitrate or mercurous nitrate may be used as precipitating agents. The precipitate is washed with a solution of the salt used for the precipitation. In the case of mercurous chromate, ignition converts the precipitate into chromic oxide—Cr_2O_3.

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[1] L. Schulerud, *Journ. prakt. Chem.* (2), **19**. 36, 1890.

[2] W. J. Sell, *Chem. News*, **54**. 299, 1886; A. Carnot, *Compt. Rend.*, **107**. 997, 1888.

[3] Bromine is a favourite oxidising agent. It does not attack platinum. R. von Wagner, *Deut. Ind. Ztg.*, **19**. 114, 1878; *Dingler's Journ.*, **218**. 332, 1875; **219**. 544, 1876; P. Waage, *Zeit. anal. Chem.*, **10**. 206, 1871; *Chem. News*, **25**. 282, 1872; H. Kämmerer, *Ber.*, **4**. 218, 1871; E. Reichardt, *Arch. Pharm.* (3), **5**. 1, 1876; G. Vulpius, *ib.* (3), **5**. 422, 1876.

[4] W. Gibbs, *Amer. J. Science* (2), **39**. 58, 1865.

[5] If the solution also contains chlorides, nitric acid must not be used in a platinum dish.

[6] F. H. Storer (*Proc. Amer. Acad.*, **4**. 342, 1869; *Amer. J. Science* (2), **45**. 190, 1868) used a mixture of potassium chlorate and nitric acid for oxidising chromium salts—B. Pawolleck, *Ber.*, **16**. 3008, 1883.

[7] For the reduction of chromic by acetic acid, see H. Basset, *Chem. News*, **79**. 157, 1899. "Small quantities of acetone, aldehyde, etc., are present in the inferior (grades of) acid."

[8] Barium nitrate or chloride furnish rather high results, and are not so satisfactory as the acetate—F. L. Langmuir, *Ueber die quantitative Bestimmung des Chroms auf gewichtsanalytischen und kolorimetrischen Wege*, Freiburg i. Br., 1906.

[9] If the barium acetate be added too quickly, barium acetate, etc., will be carried down with the chromate—R. H. Richards, *Chem. News*, **21**. 198, 1870.

[10] A. H. Pearson (*Chem. News*, **21**. 198, 1870) recommends a solution of ammonium acetate for the washing.

[11] The precipitate is very awkward to filter through paper.

[12] Use very gentle suction. If strong suction be applied, the felt gets choked, and subsequent filtration and washing will be very slow.

[13] It will be remembered that vanadium will be precipitated as barium vanadate, if this metal be present—A. Carnot, *Compt. Rend.*, **104**. 1803, 1887.

[14] The edges near the crucible sometimes appear green. This is due to a slight reduction by dust and alcohol. When heated in the open crucible, the green colour gradually disappears.

[15] K. Zulkowsky, *Journ. prakt. Chem.* (2), **103**. 351, 1868; L. Crismer, *Ber.*, **17**. 642, 1884.

§ 251. The Gravimetric Determination of Chromium as Chromic Oxide

Chromium is most easily and quickly determined by volumetric methods. The gravimetric process is only employed in special cases. If the chromium be in solution in the lower state of oxidation, it can be precipitated by the addition of a slight excess of ammonia in the presence of ammonium salts;[1] of freshly prepared ammonium sulphide to the boiling solution; or of hydrazine sulphate.[2] Filter, wash, calcine, and weigh as chromic oxide—Cr_2O_3. Details of the procedure are as follows:—

Reduction of Chromates.—If chromates be present, they must be reduced to a form suitable for treatment by this process. Boil the solution with 10 c.c. of hydrochloric acid, and 10 c.c. of alcohol; and continue the boiling until all the alcohol has been expelled. Sulphurous acid and sulphites are also excellent reducing agents. Jannasch and Mai[3] reduce the solution by the addition of 5 c.c. of hydrochloric acid and a couple of grams of hydroxylamine hydrochloride. This, later on, facilitates the precipitation and washing. Slightly better results are obtained with sulphuric acid[4] and hydroxylamine hydrochloride. Suppose that 25 c.c. of a solution of potassium chromate be under investigation, acidify the cold solution with 1 to 5 c.c. of dilute sulphuric acid, and add 1 gram of hydroxylamine hydrochloride.[5]

The Precipitation.—Add a slight excess of ammonia,[6] and boil the solution to drive off the excess of ammonia. Filter quickly while still hot, and wash with a dilute solution of ammonium nitrate as indicated for alumina (page 183). The precipitate is dissolved in hydrochloric acid and again precipitated with ammonia, etc., as just described.[7]

Ignition.—The wet precipitate is placed in a platinum crucible, and the temperature gradually raised so as to prevent small particles of the precipitate being projected from the crucible. After heating over the Bunsen's flame, finish the ignition over the blast. Weigh as Cr_2O_3.

The following numbers were obtained with one precipitation, using the equivalent of 0·1034 grm. of Cr_2O_3, 2 c.c. of the tannin solution, 1 c.c. of sulphuric acid, and 1 grm. of hydroxylamine hydrochloride:

Cr_2O_3 found . . .	0·1033	0·1031	0·1034	grm.
Error	−0·10	−0·29	−0·00	per cent.

Errors.—As a matter of fact, the results are generally high, possibly owing to the formation of a little alkaline chromate. The alkalies come from the reagents, imperfect washing, etc.[1] Genth[2] recommends boiling the precipitate with sulphurous acid before it is weighed, in order to make sure that the chromates are reduced; Clouet[3] recommends boiling the precipitate with alcohol; and Clark[4] suggests removing the chromates by washing with dilute acetic acid, and estimating them by titration with Mohr's salt; the chromates may be also estimated colorimetrically. With the method described in the text there is no need for any of these methods of purification.

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[1] M. Z. Jówitschitsch, *Monats. Chem.*, **34**. 225, 1913.

[2] T. Hanus and T. Lucas, *Chem. Ztg.*, **36**. 1134, 1912.

[3] P. Jannasch and J. Mai, *Ber.*, **26**. 1786, 1893; P. Jannasch and F. Rühl, *Journ. prakt. Chem.* (2), **72**. 10, 1905; C. Friedheim and P. Hasenclever, *Zeit. anal. Chem.*, **44**. 594, 1905.

[4] It is not advisable to use less than 1 c.c. of dilute sulphuric acid. If too little acid be employed, the reduction is disturbed by a side reaction attended by the development of nitrous fumes, and the formation of a brown instead of a violet-coloured solution.

[5] The addition of 2 c.c. of a 2·5 per cent. solution of tannin before the addition of the ammonia gives a precipitate much easier to filter and wash—R. E. Divine, *Journ. Soc. Chem. Ind.*, **24**. 11, 1905.

[6] Chromium hydroxide is soluble in an excess of ammonia, forming a red solution. This can easily be demonstrated by adding ammonia to a dilute solution of a chromium salt. No precipitate can be observed until the solution has been boiled a long time.

[7] Take care in the washing, or the results may be 2 per cent. high when only one precipitation is made.

Hence, the two important errors in this determination arise from the solubility of the hydroxide in ammonia, and the presence of alkalies in the calcined oxide. If the excess of ammonia be expelled by boiling, the precipitate becomes slimy, and difficult to wash, and so aggravates the second source of error.[5] The effect of a slight excess of ammonia need not be feared when hydroxylamine is used, because hydroxylamine, not free ammonia, will be present, and chromium hydroxide is not appreciably soluble in this menstruum. Again, the addition of tannin enables the precipitate to be more readily washed, and thus facilitates the removal of alkalies.

It is interesting to note that the precipitated chromium hydroxide may be coloured either violet, or green, or intermediate tints. The green precipitate[6] is commonest with the alcohol reduction, the violet with the hydroxylamine reduction. The violet precipitate is nearly always obtained by the method described in the text. If tannin is present, the precipitate appears grey. The green precipitate seems to have a greater avidity for alkalies than the violet-coloured one, and thus gives rather higher results.

Effect of Phosphoric Acid.—When phosphoric acid is present, chromium phosphate will be precipitated.[7] In that case, fuse the dried precipitate with sodium carbonate and a little sodium nitrite. Dissolve the melt in water acidified with nitric acid, and precipitate the phosphoric acid with ammonia and magnesia mixture. The chromium may be determined by difference, or precipitated from the filtrate as barium chromate, or determined volumetrically.

§ 252. The Volumetric Determination of Vanadium.

One method for the determination of vanadium is based on the reduction of vanadium pentoxide—V_2O_5—by sulphur dioxide to vanadium tetra-oxide—V_2O_4,—and the re-oxidation of the latter by a standard solution of potassium permanganate.[8]

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[1] T. Wilm, *Ber.*, **12.** 2223, 1887; *Chem. News*, **41.** 222, 1880; F. P. Treadwell, *Ber.*, **15.** 1392, 1880. A. Souchay (*Zeit. anal. Chem.*, **4.** 66, 1865) thinks that the high results are due to the action of the ammonia on the glass vessels.

[2] F. A. Genth, *Amer. J. Science* (2), **5.** 418, 1873.

[3] P. Clouet, *Ann. Chim. Phys.* (4), **16.** 90, 1849.

[4] J. Clark, *Chem. News*, **24.** 304, 1871.

[5] J. Hanus and J. Lukas (*Inter. Cong. App. Chem.*, 8. 209, 1912) quantitatively precipitate chromium from neutral or alkaline solutions—containing chromates, or chromic salts—by means of hydrazine hydrate or some of the derivatives of hydrazine—hydrazine sulphate, phenylhydrazine, thiosemicarbazide. The precipitation is more rapid and complete in the presence of ammonium chloride, and thiosemicarbazide gives best results.

[6] The violet hydroxide is possibly $Cr(OH)_3$; the green, $Cr_2O(OH)_4$.

[7] H. Baubigny, *Bull. Soc. Chim.* (2), **41.** 291, 1884; *Chem. News*, **50.** 18, 1884.

[8] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **20.** 461, 1898; A. Bettendorff, *Pogg. Ann.*, **160.** 126, 1877; C. Czudnowicz, *ib.*, **120.** 17, 1863; C. Rammelsberg, *Ber.*, **1.** 158, 1868; B. W. Gerland, *ib.*, **10.** 1513, 1516, 1877; O. Manasse, *Liebig's Ann.*, **240.** 23, 1887; *Zeit. anal. Chem.*, **32.** 225, 1893; O. Lindemann, *ib.*, **18.** 99, 1879; F. A. Genth and G. von Rath, *Chem. News*, **53.** 218, 1886; **34.** 78, 1896; J. R. Cain, *Bull. Bur. Standards*, **7.** 377, 1911; E. de M. Campbell and C. E. Griffin, *Journ. Ind. Eng. Chem.*, **1.** 661, 1909; G. Auchy, *ib.*, **1.** 455, 1910; G. Edgar, *Amer. J. Science* (4), **25.** 332, 1908; F. A. Gooch and L B Stookay, *ib.* (4), **14.** 369, 1902; F. A. Gooch and R. D. Gilbert, *ib.* (4), **15.** 389, 1903; F. A. Genth, *ib.* (3), **12.** 32, 1876; F. A. Gooch and G. Edgar, *ib.* (4), **25.** 233, 1908; *Ber.*, **38.** 600, 1905;

Suppose we have to deal with the solution remaining after the determination of chromium (page 473).[1] The boiling solution is reduced with sulphur dioxide, and the excess of sulphur dioxide is expelled by passing a current of carbon dioxide through the solution, which is then titrated, while hot, with a dilute solution of potassium permanganate—approximately $\frac{1}{100}$-N, that is, 0·3163 grm. of $KMnO_4$ per litre[2]—until a permanent pink colour is obtained.

If but a small quantity of permanganate be employed, verify the presence of vanadium as follows:—Evaporate the solution to dryness in order to expel the sulphuric acid; take up the residue with 3–4 c.c. of water; acidify the solution with a few drops of nitric acid; and add two or three drops of hydrogen peroxide. A brownish-red colour indicates vanadium. If the solution be titrated cold, the end point is not so sharp.[3]

After the titration, reduce the boiling solution with a current of sulphur dioxide, when $V_2O_2(SO_4)_3$ passes to $V_2O_2(SO_4)_2$; or, generalised:

$$V_2O_5 + SO_2 \rightarrow SO_3 + V_2O_4.$$

Boil the solution while a rapid current of carbon dioxide is passing through until the escaping gas no longer decolorises a solution of potassium permanganate. Repeat the titration on the hot solution. The reduction and titration can be repeated once again. The last two results will probably be lower than the first. The mean of these titrations represents the vanadium in the given solution.

Hillebrand's Correction for Excess of Chromium.—If over 0·005 grm. of chromium be present, a correction must be made, since an appreciable quantity of the permanganate is needed for oxidising the chromium. Make a solution of potassium chromate containing the same amount of chromium as the solution under investigation. Reduce with sulphur dioxide as indicated for vanadium, and titrate with the standard permanganate. The amount of permanganate used must be subtracted from that consumed in titrating for vanadium, and the difference represents that used in converting $V_2O_4 \rightarrow V_2O_5$. It is perhaps easier to determine the chromic and vanadic acids volumetrically by the following process than to apply these corrections.

Volumetric Determination of Chromic and Vanadic Acids.—It might be added that Edgar[4] has devised a process for the simultaneous determination of these two compounds. The process is based on the fact that hydrobromic acid will reduce vanadic acid to vanadium tetroxide—$V_2O_5 \rightarrow V_2O_4$—and chromic acid to chromic oxide—$2CrO_3 \rightarrow Cr_2O_3$; and hydriodic acid will reduce vanadium tetroxide to the trioxide—$V_2O_4 \rightarrow V_2O_3$, and leave chromic oxide unaffected. The mixture of

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E. P. Alvarez, *Chem. Ztg.*, **33**. 149, 1909; P. Slawik, *ib.*, **36**. 171, 1912; E. Campagne, *Bull. Soc. Chim.* (3), **31**. 962, 1906; *Compt. Rend.*, **137**. 570, 1898; A. Ditte, *ib.*, **101**. 698, 1885; C. Matignon and P. Monnet, *ib.*, **134**. 542, 1902; W. Heike, *Stahl Eisen*, **25**. 1357, 1905; C. Hensen, *Kritische Untersuchung der Vanadin Bestimmungsmethoden*, Aachen, 36, 1909. H. E. Roscoe (*Journ. Chem. Soc.*, **11**. 928, 1871) considered the process by zinc reduction not reliable. D. J. Demorest, *Journ. Ind. Eng. Chem.*, **4**. 249, 895, 1912; J. R. Cain and J. C. Hostetter, *ib.*, **4**. 250, 1912; J. R. Cain and D. J. Demorest, *ib.*, **4**. 256, 1912; F. Garratt, *ib.*, **4**. 256, 1912.

[1] If molybdenum and arsenic be present, the solution, after the determination of chromium (page 473), is acidified with sulphuric acid, and treated with hydrogen sulphide (page 277), when both arsenic and molybdenum together with traces of platinum from the crucible are precipitated. Boil the filtrate to expel hydrogen sulphide.

[2] 1 grm. $KMnO_4$ corresponds with 2·883 grms. V_2O_5 for the oxidation $V_2O_4 \rightarrow V_2O_5$.

[3] The temperature of the solution being titrated is of importance; the best temperature is between 70° and 80°. If the titration be conducted at too low a temperature, the end point is not sharp enough, and if at too high a temperature, the permanganate may be reduced by the hot sulphuric acid solution of manganous sulphate, as shown by A. C. Sarkar and J. M. Dutta (*Zeit. anorg. Chem.*, **67**. 225, 1910).

[4] G. Edgar, *Amer. J. Science* (4), **26**. 333, 1908.

chromic and vanadic oxides (about 0·2 grm.) is boiled in a flask *A*, fig. 154, with 15 c.c. of hydrochloric acid, and 2 grms. of potassium bromide. The flask is arranged so that a slow current of hydrogen from a Kipp's apparatus and wash-bottle, *B*, passes while the solution is being boiled. The bromine vapour evolved owing to the reaction: $V_2O_5 + 2CrO_3 + 8HBr = V_2O_4 + Cr_2O_3 + 4H_2O + 8Br$, is led through a pair of Wölbling's flasks, *C*, containing an alkaline solution of potassium iodide. When the reaction is over, the contents of the absorption bulbs are washed into an Erlenmeyer's flask; the solution is acidified with hydrochloric acid; and the free iodine, liberated by the action of the bromine on the potassium iodide—$Br_2 + 2KI = 2KBr + I_2$—is titrated with sodium thiosulphate in the usual manner.

Two grams of potassium iodide, 15 c.c. of hydrochloric acid, and 3 c.c. of syrupy phosphoric acid are now added to the solution in the boiling flask, and the distillation repeated as before in a current of hydrogen. The absorption flasks are charged as before, and the iodine liberated by the reaction—$V_2O_4 + 2HI = V_2O_3 + H_2O + I_2$—is absorbed by the alkaline potassium iodide, and titrated as before. The second titration furnishes data for calculating the amount of vanadic acid in the original solution; and the first and second titrations give data for calculating the amount of chromic acid.

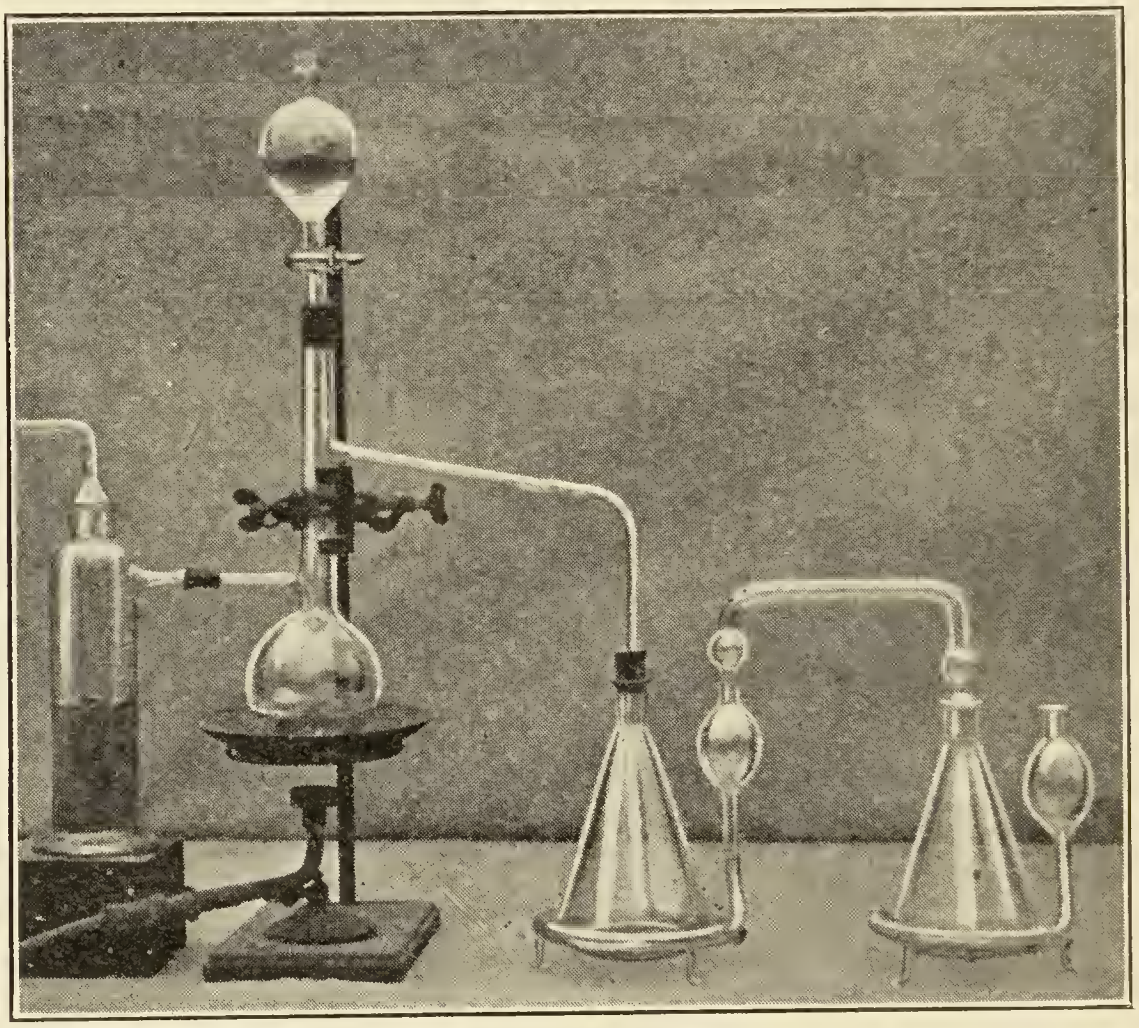

FIG. 154.—Simultaneous determination of chromic and vanadic acids.

Volumetric Determination of Vanadium and Molybdenum.[1]—If a solution of molybdic and vanadic acids be treated with sulphur dioxide, the vanadic acid, V_2O_5, is alone reduced to vanadium tetroxide, V_2O_4, provided the solution contains no more than 0·2 grm. of molybdic acid per 50 c.c., and approximately 1 c.c. of free sulphuric acid. When the reduction is complete, pass a current of carbon dioxide through the boiling liquid to drive off the sulphur dioxide. The vanadium tetroxide can be titrated in the usual manner with $\frac{1}{10}$N-potassium permanganate. Then pass the solution through a reductor containing amalgamated zinc, and received into 50–60 c.c. of a 10 per cent. solution of ferric alum; add 8–10 c.c. of syrupy phosphoric acid to decolorise the iron salt, and titrate with $\frac{1}{10}$-N potassium permanganate as before. The permanganate required for the latter titration includes that required for converting the V_2O_2 to V_2O_5, and for the conversion Mo_2O_3 to $2MoO_3$; the former is three times the amount consumed for the $V_2O_4 \rightarrow V_2O_5$ titration.

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[1] G. Edgar, *Amer. J. Science* (4), **25**. 332, 1908.

Volumetric Determination of Vanadium and Iron.[1]—If a mixed solution of ferric and vanadic oxides, acidified with a little sulphuric acid, be treated in a similar manner, the first titration (after the sulphur dioxide reduction) corresponds with the conversion of V_2O_4 to V_2O_5, and of $2FeO \rightarrow Fe_2O_3$; and the second titration (after the zinc reduction) with $V_2O_2 \rightarrow V_2O_5$, and of $2\ FeO \rightarrow Fe_2O_3$. Hence, with $\frac{1}{10}$N-permanganate, the difference between the two titrations multiplied by 0·00456 gives the amount of vanadic acid originally present, and the amount of iron can then be calculated from either titration.

§ 253. The Gravimetric Separation of Chromium and Vanadium.

Instead of applying the colorimetric process for chromium, followed by the volumetric process for vanadium, these two constituents can be determined gravimetrically[2] in the following manner:—Hydrochloric acid, if present, is expelled from the solution by repeated evaporation with nitric acid.[3] The solution is just neutralised with sodium hydroxide, and acidified with acetic acid, or lead acetate is added to the boiling solution. Boil three or four minutes. The voluminous precipitate of lead chromate and lead vanadate[4] soon settles, provided too great an excess of lead acetate has not been added.[5]

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[1] G. Edgar, *Amer. J. Science* (4), **26**. 79, 1908.

[2] The chromium may be separated, if desired, by reducing the solution with sulphurous acid. Pour the boiling solution slowly, with constant stirring, into a boiling solution of sodium hydroxide containing 100 grms. of solid per litre. Boil, filter, and wash. Neutralise with nitric acid (blue litmus just red) and add a few drops of sodium hydroxide; boil and filter. The precipitate contains the chromium, nickel, iron, manganese and copper if present. A trace of chromium may also pass into the filtrate, since the manganese peroxide formed during the boiling of the solution oxidises the chromium to soluble chromate (J. R. Cain, *Journ. Ind. Eng. Chem.*, **3**. 476, 1911; **4**. 17, 1912; A. A. Noyes and W. C. Bray, *Tech. Quart.*, **21**. 14, 1908). Most of the vanadium passes into the filtrate, though a little may be retained by the precipitate, and two or three precipitations may be needed to get all the vanadium in the filtrate (W. Trautmann, *Stahl Eisen*, **30**. 1802, 1910). This is attended by the passage of a relatively large amount of chromium into the filtrate. Vanadium, if present, is generally precipitated by ammonia along with aluminium, hydroxide, etc. Warm the precipitate with ammonium phosphate on a water bath. Ammonium vanadate passes into solution, and aluminium and ferric phosphates remain insoluble. Wash the precipitate with ammonium chloride solution—O. Bettendorff, *Pogg. Ann.*, **160**. 126, 1877.

[3] If the fused cake obtained in, say, the barium carbonate precipitation is under treatment, dissolve the mass in hot water; add 2–3 c.c. of hydrogen peroxide to the filtrate in order to destroy any nitrates present and prevent their reducing chromium and vanadium. Boil 10–15 minutes to destroy the hydrogen peroxide and prevent its reducing chromic acid when the solution is acidified (perchromic acid, of course, would be first formed, but this rapidly decomposes). In case the cake is under treatment, it is well to make sure the insoluble matter does not contain chromium by re-fusing it with the mixture (sodium carbonate 4; sodium nitrite 1). If the fused cake is white when cold, chromium is absent; if yellow, determine the chromium colorimetrically.

[4] T. Fischer, *Ueber die Bestimmung von Vanadinsäure*, Berlin, 1894; G. Sefström, *Pogg. Ann.*, **21**. 43, 1831; J. J. Berzelius, *ib.*, **22**. 1, 1831; H. E. Roscoe, *Liebig's Ann. Suppl.*, **8**. 95, 1872; E. Claassen, *Amer. Chem. Journ.*, **7**. 349, 1886; H. Cormimbœuff, *Ann. Chim. Anal. App.*, **7**. 258, 1902. H. F. Watts (*Western Chem. Met.*, **5**. 408, 1909; *Chem. News*, **101**. 34, 1910) precipitates lead vanadate in a solution just acid with nitric acid and containing 1 to 2 grms. of sodium acetate. The precipitate is dissolved in dilute nitric acid, and the lead and nitric acid removed by repeated evaporation with sulphuric acid.

[5] If the sodium carbonate fusion be treated with a slight excess of dilute nitric acid (1 : 1) and boiled vigorously a few minutes to expel the carbon dioxide, just neutralised with sodium

Separation of the Chromium.—Evaporate the solution to about 30 c.c. on a water bath. Add 2 grms. of solid potassium carbonate; evaporate the solution to dryness; take up the residue with a little hot water; let the precipitate settle, and decant the clear liquid through a filter paper. Wash the filter paper with water, and then wash any precipitate which may be on the paper back into the vessel containing the bulk of the precipitate. Evaporate the filtrate down to about 15 c.c. and repeat the operations just described. If the precipitate is white,[1] wash the precipitate; if yellowish, repeat the treatment with potassium carbonate. The filtrate contains the chromic acid. Acidify the solution with acetic acid—carbon dioxide is evolved, and lead chromate is precipitated. The solution is heated to boiling, and more lead acetate is added until all the chromium is precipitated, and the precipitate is treated gravimetrically as indicated on page 325; or the lead chromate precipitate is collected on the asbestos mat in a Gooch's crucible, and then dissolved in hot dilute hydrochloric acid (1 : 4). The solution is cooled; treated with an excess of ferrous sulphate; and titrated with standard bichromate or permanganate as directed on pages 198 and 453.

Precipitation of the Vanadium.—The precipitate of lead carbonate and lead vanadate[2] is dissolved in nitric acid; evaporated to dryness; and the solution taken up with dilute hydrochloric acid. The lead is precipitated as sulphide. Filter. Evaporate the solution down to a small volume, and treat it with concentrated nitric acid; evaporate to dryness; filter into a platinum crucible; and after calcination (fusion) weigh as V_2O_5. (For the effect of chlorides, see page 472.) The vanadium may here be determined volumetrically (page 480) or colorimetrically.

§ 254. The Rapid Determination of Vanadium—Cain and Hostetter's Process.

In the absence of titanium, the hydrogen peroxide colorimetric process described for titanium can be applied, *mutatis mutandis*, to vanadium.[3] Gregory's colorimetric process[4] can be used for the colorimetric determination of vanadium in the presence of titanium. It is based on the orange coloration which is developed when an acid solution of vanadic sulphate is brought in contact with strychnine. The solution is at first coloured deep violet; this gradually changes to an intense orange. The intensity of the orange coloration depends upon the amount of vanadium in the solution. The process gives fairly satisfactory

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hydroxide, and 2 c.c. of nitric acid (1 : 1) per 100 c.c. of solution, followed by, say, 20 c.c. of a 20 per cent. solution of lead nitrate, lead chromate alone is precipitated from the cold solution containing chromium, vanadium, and uranium, according to A. A. Noyes, W. C. Bray, and E. B. Spear (*Tech. Quart.*, **21**. 14, 1908; *Journ. Amer. Chem. Soc.*, **30**. 481, 1908; R. Cain, *Journ. Ind. Eng. Chem.*, **4**. 17, 1912), only 0·0001–0·0003 grm. of chromium remains in solution, and no precipitate was obtained with solutions containing 0·1 grm. of vanadium. Lead vanadate is sparingly soluble and can be precipitated quantitatively in presence of a weaker acid—acetic acid and ammonium acetate. Lead uranate is precipitated from neutral or slightly alkaline solutions. If the filtrate is afterwards required, the lead is removed with hydrogen sulphide.

[1] The ether and hydrogen peroxide test for chromium can be made. G. Werther, *Journ. prakt. Chem.* (1), **83**. 195, 1861. According to F. H. Storer, this reaction detects 1 part of potassium chromate in 40,000 parts of water. W. J. Karslake, *Journ. Amer. Chem. Soc.*, **31**. 250, 1909; C. Reichard, *Zeit. anal. Chem.*, **40**. 577, 1901; M. Martinon, *Bull. Soc. Chim.* (2), **45**. 862, 1886.

[2] R. Holverscheit, *Ueber die quantitative Bestimmung des Vanadins und die Trennung der Vanadinsäure von Phosphorsäure*, Berlin, 21, 1890.

[3] V. von Klecki, *Zeit. anorg. Chem.*, **5**. 374, 1894; L. Maillard, *Bull. Soc. Chim.* (3), **23**. 422, 559, 1900; *Chem. News*, **82**. 19, 1900; L. C. Barreswil, *Compt. Rend.*, **16**. 1085, 1843; G. Werthier, *Journ. prakt. Chem.* (1), **83**. 195, 1861; C. Reichard, *Zeit. anal. Chem.*, **40**. 577, 1901; **42**. 95, 293, 1903.

[4] A. W. Gregory, *Chem. News*, **100**. 221, 1909; J. R. Cain and J. C. Hostetter, *Journ. Ind. Eng. Chem.*, **4**. 250, 1912. The lower oxides of vanadium do not give the colour test. For other colour reactions see L. Levy, *Compt. Rend.*, **103**. 1195, 1886; C. Matignon, *ib.*, **138**. 82, 1904; C. Reichard, *l.c.*; V. von Klecki, *l.c.*; C. Laar, *Ber.*, **15**. 2086, 1882; O. N. Witz, *Dingler's Journ.*, **250**. 271, 1883; *Bull. Soc. Chim.* (2), **45**. 309, 1886.

results in the presence of titanium, molybdenum, and tungsten, but it is not satisfactory in the presence of iron. Of course the iron can be removed by fusion with sodium carbonate, and extraction with water. The use of concentrated sulphuric acid is a very unpleasant feature in this process. The following volumetric method, due to Cain and Hostetter, enables a vanadium determination to be made in about half an hour. The process is based on the fact that vanadic acid can be quantitatively precipitated by ammonium phosphomolybdate, and the vanadium reduced to the quadrivalent condition by hydrogen peroxide without interference from the associated iron and molybdenum. The solution can then be titrated with permanganate in the usual manner.

The solution under investigation in the Erlenmeyer's flask—containing possibly iron, titanium, chromium, vanadium, manganese, etc.—is heated to boiling and treated with ammonia; the precipitate is washed once or twice by decantation, and dissolved in nitric acid (sp. gr. 1·135). Boil the solution until it is free from fumes, and oxidise it with potassium permanganate. Dissolve the precipitate by treatment with sodium sulphite, and boil the mixture until it is free from nitrous fumes. Nearly neutralise the solution with ammonia, and add an amount of a solution of sodium phosphate[1] equivalent to ten times as much phosphorus as there is vanadium present. Heat the solution to boiling, and add sufficient ammonium molybdate (page 595) to precipitate all the phosphorus added as sodium phosphate. Agitate the solution for about a minute. The precipitate, which settles rapidly, is washed three times by decantation with hot (80°) acid ammonium sulphate solution.[2] The washing liquid is filtered by suction through an asbestos-packed Gooch's crucible. The last washing should be decanted as completely as possible from the precipitate in the flask, and the filter sucked dry. Change the filtration flask, and draw hot concentrated sulphuric acid through the Gooch's crucible by suction. This dissolves the precipitate. Transfer the sulphuric acid solution to the flask in which the precipitation was made. Wash the filtration flask with concentrated sulphuric acid. Every 0·01 grm. of phosphorus requires a final volume of 5 to 8 c.c. of the sulphuric acid. Heat the contents of the flask until the precipitate is all dissolved, add a few drops of nitric acid (1 : 25), and in two or three minutes, when the fumes are coming off vigorously, remove the flask from the hot plate. When cold, add 3 per cent. hydrogen peroxide solution, in small quantities at a time, with vigorous shaking after each addition, until the solution assumes a deep brown colour owing to the action of the peroxide on the molybdate. The brown coloration gives way to a clear green or blue.[3] Put the flask on the hot plate, and when the solution has been fuming four or five minutes, cool, add sufficient water to give an acidity 1 to 5 by volume,[4] and titrate at a temperature between 70° and 80°, as indicated in § 252, page 481.

It will be remembered that, if appreciable amounts of vanadium are present, the colorimetric process for titanium will be erroneous. The volumetric process is not sensitive enough for the traces of vanadium usually found in British fireclays, unless relatively large quantities are taken for analysis.

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[1] Sodium Phosphate Solution.—Dissolve 124 grams of $Na_2HPO_4.12H_2O$ in a litre of water. One c.c. will precipitate 0·001 grm. of vanadium, and it is equivalent to nearly 0·01 grm. of phosphorus. G. P. Baxter, *Amer. Chem. Journ.*, **28.** 301, 1902.

[2] Acid Ammonium Sulphate Solution.—Mix 15 c.c. of aqueous ammonia (sp. gr. 0·9) with 1000 c.c. of water and 25 c.c. of sulphuric acid (sp. gr. 1·84).

[3] If the vanadium be not reduced, traces of nitric acid are probably present in the solution, since this acid readily oxidises quadrivalent vanadium. The nitric acid must be removed by the fuming process.

[4] If the solution has a greater acidity than 1 : 2, the end point will be uncertain because of the deep yellow colour which quinquevalent vanadium imparts to concentrated sulphuric acid. A dilution of 1 : 5 gives a sharp end point.

§ 255. The Simultaneous Determination of Small Quantities of Titanium and Vanadium colorimetrically.

Principle of the Method.[1]—When dilute acidified solutions of titanium and of vanadium sulphates, coloured by the addition of hydrogen peroxide, are measured in Lovibond's tintometer, and the results with the red rays plotted on squared paper, curves resembling two of the three shown in fig. 155 are obtained. If titanium solutions are coloured with Fenton's acid (p. 468)[2]—dihydroxymaleic acid, $C_4H_4O_6 . 2H_2O$—the curve, also shown in fig. 155, is produced.[3] The curves for the red rays in duplicate experiments are quite concordant, and the readings for the curves fig. 155 do not deviate more than 0·02 on Lovibond's scale. With practice, too, the variations can be reduced to 0·01. The yellow rays are more difficult to manage, because the eye requires more practice to detect differences of the yellow ray. Hence it is best to confine the attention to the intensity of the red ray.

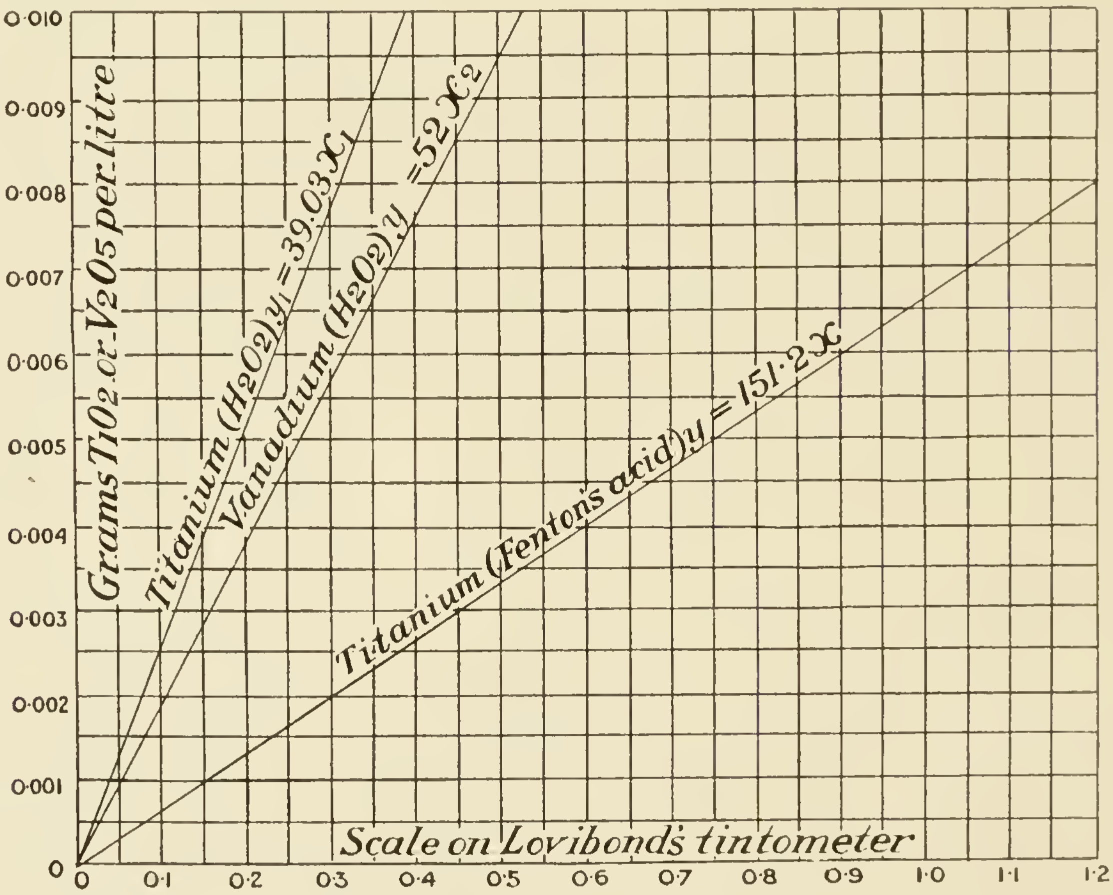

FIG. 155.—Intensity of red rays in solutions of vanadium and titanium coloured with hydrogen peroxide and Fenton's acid (1" trough).

The intensities of the red and yellow tints of mixed solutions of titanium are directly proportional to the amounts of each of these elements present in the solution. The coloration of solutions of titanium sulphate with Fenton's acid is not affected by the presence of vanadium; consequently, the intensity of the colour of a given solution of titanium with this acid enables the amount of titanium to be computed graphically from the charts—drawn on a larger scale than fig. 155—or from the equation of the curve:

$$y = 151·20x \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

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[1] H. J. H. Fenton, *Journ. Chem. Soc.*, **9**. 1064, 1908 ; J. W. Mellor, *Trans. Eng. Cer. Soc.*, **12**. 18, 1912.

[2] For the coloration of titanium solutions with phenols, naphthols, phenolcarboxylic acids, see O. Hauser and A. Lewite, *Ber.*, **45**. 2480, 1912 ; V. Lehner and W. G. Crawford, *Inter. Cong. App. Chem.*, **8**. 285, 1912 ; *Journ. Amer. Chem. Soc.*, **35**. 138, 1913.

[3] With more concentrated solutions the curves take on the exponential form $y = ae^{-bx}$ and the error is greater.

where y denotes the intensity of the red ray on Lovibond's scale (with the "inch" trough), and x the amount of titanium oxide, TiO_2, expressed in grams, per litre of solution. It is very important to keep the conditions constant, because the tint is liable to vary with small modifications. This is the weakest stage of the process.

When the amount of titanium in the mixture has been so determined, the corresponding value of the red ray on Lovibond's scale can be computed for the hydrogen peroxide coloration either graphically (fig. 155) or from the equation of the curve:

$$y_1 = 39{\cdot}03x_1 \qquad . \quad . \quad . \quad . \quad . \qquad (2)$$

where x_1 denotes the amount of titanic oxide in grams per litre, and y_1 the corresponding effect on the red ray on Lovibond's scale. Since the intensity of the red ray for the mixed solution of titanium and vanadium sulphates can be determined directly, the effect due to the titanium can be deducted, and the remainder represents the intensity of the red tint produced by the vanadium. The corresponding amount of vanadium can be computed graphically (fig. 155) or from the equation of the curve:

$$y_2 = 52{\cdot}00x_2 \qquad . \quad . \quad . \quad . \quad . \qquad (3)$$

where y_2 denotes the reading on Lovibond's scale for a solution containing x_2 grams of vanadium per litre—coloured by hydrogen peroxide.[1]

Conduct of the Analysis.—During the analysis of a silicate—say a fireclay—the vanadium and titanium oxides will be found with the iron and aluminium oxides in the ammonia precipitate. This is washed, calcined, and weighed in the usual way—page 183. The mass is then fused with eight times its weight of sodium pyrosulphate, and the resulting cake, when cold, is taken up with water (page 186) and treated by Gooch's process (page 208) or by the ether process (page 456) to remove the iron.[2] The solution is acidified with sulphuric acid,[3] and an aliquot portion—say, one-half—is treated with hydrogen peroxide as indicated on pages 204–6. The colour of the solution is measured in Lovibond's tintometer (page 84). The remaining aliquot portion of the solution is treated in a similar way, but about 0·2 gram of Fenton's acid[4] is added instead of hydrogen peroxide. Let the solution stand about an hour,[5] and then read its colour in Lovibond's tintometer.

EXAMPLE.—The "ammonia" precipitate furnished by a gram of fireclay was treated as described above, and the solution made up to 200 c.c. Half of this solution was treated with Fenton's acid and made up to 200 c.c. This solution gave 1·25 red units with Lovibond's tintometer. From equation (1), when $y = 1{\cdot}25$, $x = 0{\cdot}00826$, hence the solution contained the equivalent of 0·00826 gram of titanic oxide per litre; or 0·0033 gram per 400 c.c., or 0·0033 gram of titanic oxide per gram of clay. Again, from equation (2), when $x = x_1 = 0{\cdot}00826$, $y_1 = 0{\cdot}32$: hence, since the combined titanium and vanadium give 0·36 red units, $0{\cdot}36 - y_1 = 0{\cdot}36 - 0{\cdot}32 = y_2 = 0{\cdot}04$. When $y_2 = 0{\cdot}04$, $x_2 = 0{\cdot}00077$ from (3). Consequently, if 1000 c.c. of the solution contain 0·00077 gram of vanadic oxide, 400 c.c., corresponding with 1 gram of clay, contain 0·0003 gram of vanadic oxide. Hence, the clay contained :

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[1] The constants in the equation naturally change if a different observation trough is used, and they possibly also vary a little with different observers. The method of computing the constants for the equations is described in J. W. Mellor, *Higher Mathematics for Students of Chemistry and Physics*, London, 322, 1909. There is no need to use the equations if careful graphs are drawn, of course on a larger scale than fig. 155.

[2] The iron oxide can be determined by dissolving it in acid, etc., as usual.

[3] If the solution be not distinctly acid, the vanadium does not develop its proper colour; in fact, the strength of the acid can be so reduced that the colour shows with titanium but not with vanadium.

[4] The acid is not yet on the market, but it will no doubt soon find its way in commerce. It is best to add the solid as described in the text; if much more acid be used in one experiment than in another, the tints will be slightly different.

[5] The colour develops gradually unless the solution is warmed a little. The rate of change of the colour after standing an hour is slow enough not to interfere with the accuracy of the work.

Vanadic oxide (V_2O_5)	0·03 per cent.
Titanic oxide (TiO_2)	0·33 per cent.

§ 256. The Separation of Uranium.[1]

The filtrate from the silica ; the pyrosulphate fusion ; or from the hydrogen sulphide precipitation[2] is evaporated to about 100 c.c. and treated with an excess of ammonia,[3] ammonium carbonate, and afterwards with ammonium sulphide.[4] The solution is allowed to stand overnight in a corked flask, filtered, and washed with water containing ammonium carbonate and sulphide in solution. The precipitate contains the beryllium, titanium, zirconium, aluminium hydroxides,[5] and the hydroxides of the rare earths, also the cobalt, zinc, ferric, and manganese sulphides, if present. If much alkalies, alkaline earths, iron, or manganese be present, dissolve the precipitate in acid and repeat the precipitation. Collect the filtrates together. The filtrate contains all the uranium (possibly as uranyl ammonium carbonate), along with alkalies, alkaline earths, etc.

Separation of Rare Earths and Calcium from Uranium.[6]—If the rare earths be present, some may be found with the ammonium uranate. In that case, the precipitate from the ammonium sulphide is dissolved in nitric acid, and the solution evaporated to dryness. Add water ; heat the solution to boiling ; and, while boiling, add oxalic acid and a few drops of ammonium oxalate. Wash the precipitated oxalates with a weak solution of oxalic acid. The precipitate is dissolved in nitric acid ; and reserved for further examination of the rare earths.[7] The filtrate is evaporated to dryness, and ignited to destroy the oxalates, redissolved in nitric acid; after removal of all the nitric acid by repeated evaporation with sulphuric acid, the residual sulphates are dissolved in water, and two to three times the bulk of alcohol added. In the course of 12 hours, the precipitate will contain the calcium not thrown down by the oxalic treatment for the rare earths. Collect the precipitate on a filter; wash with alcohol; dry; dissolve in dilute nitric acid; and separate the rare earths from the lime by means of ammonia.[1] The alcoholic filtrate is evaporated to dryness, and ignited. The residue is dissolved in nitric acid and the uranium precipitated by ammonia in the form of ammonium uranate.[2]

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[1] F. Pisani, *Compt. Rend.*, **52.** 106, 1861 ; C. Friedel and E. Cumenge, *ib.*, **128.** 532, 1899 ; *Amer. J. Science* (4), **10.** 135, 1900 ; G. Edgar, *ib.* (4), **26.** 79, 1908 ; (4), **25.** 332, 1908 ; H. P. Foullon, *Jahrb. K. K. Geol. Reichanst.*, **33.** 23, 1887 ; C. Rammelsberg, *Chem. Centr.* (3), **15.** 806, 1884 ; C. Zimmermann, *Liebig's Ann.*, **213.** 285, 1882 ; G Alibigoff, *ib.*, **233.** 117, 143, 1886 ; *Zeit. anal. Chem.*, **26.** 632, 1887 ; H. Weber, *ib.*, **44.** 420, 1905 ; A. Remelé, *ib.*, **4.** 379, 1865 ; **26.** 631, 1888 ; R. Fresenius and E. Hintz, *ib.*, **34.** 437, 1895 ; A. Borntrager, *ib.*, **37.** 436, 1898 ; C. Winkler, *ib.*, **8.** 357, 1869 ; *Chem. News*, **43.** 153, 1881 ; A. Guyard, *ib.*, **10**, 13, 1864 ; A. C. Langmuir, *ib.*, **84.** 224, 1901 ; *Journ. Amer. Chem. Soc.*, **22.** 102, 1900 ; A. N. Finn, *ib.*, **28.** 1443, 1906 ; *Chem. News*, **95.** 17, 1907 ; O P. Fritchle, *ib.*, **82.** 258, 1900 ; *Eng. Min. Journ.*, **70.** 548, 1900 ; W. Gibbs, *Zeit. anal. Chem.*, **12.** 310, 1873 ; *Amer. J. Science*, (2), **39.** 62, 1865 ; A. Patera, *ib.* (4), **16.** 229, 1903 ; *Dingler's Journ.*, **180.** 242, 1866 ; *Zeit. anal. Chem.*, **5.** 228, 1866 ; W. Trautmann, *Zeit. angew. Chem.*, **24.** 61, 1911.

[2] Boiled to expel hydrogen sulphide, filtered to get rid of sulphur, and oxidised with nitric acid. For the hydrogen sulphide precipitation, the acidity should correspond with about 1 c.c. concentrated hydrochloric acid (sp. gr. 1·20), or 1 c.c. of concentrated nitric acid (sp. gr. 1·42), per 50 c.c. of the solution to get a clean separation from lead, cadmium, copper, etc. If much more acid be present, some lead will remain in solution, as indicated on page 274.

[3] According to W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, **78.** 43, 1890), ammonia is necessary, otherwise the earths thrown down on neutralisation of the originally acid solution will be only partially redissolved.

[4] H. Rose, *Pogg. Ann.*, **96.** 352, 1865 ; *Chem. News*, **7.** 159, 1863 ; **8.** 99, 1863 ; *Zeit. anal. Chem.*, **1.** 410, 1862 ; W. Trautmann, *Zeit. angew. Chem.*, **24.** 61, 1911 ; **25.** 19, 1912. H. Boetticher (*ib.*, **43.** 99, 1903) deals with the separation of metals precipitated with ammonium sulphide. For the basic acetate separation, see H. Rheineck, *Chem. News*, **24.** 233, 1871 ; A. Remelé, *Chem. News*, **10.** 123, 158, 1864.

[5] G. Lösekann (*Ber.*, **12.** 56, 1881) deals with the precipitation of aluminium and chromium by alkaline sulphides. See L. Storch (*ib.*, **16.** 2014, 1885) for the precipitation of iron by alkaline sulphides, and J. A. Norblad (*Bull. Soc. Chim.* (2), **23.** 64, 1875) for the separation of vanadium.

[6] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **78.** 47, 1891.

[7] The rare earths are here separated from lime by precipitating with ammonia (page 504).

§ 257. The Gravimetric Determination of Uranium as Uranium Oxide.

Evaporate the filtrate containing the uranium to dryness in order to get rid of the greater part of the ammonium carbonate. Acidify the solution with hydrochloric acid and a few drops of nitric acid; boil to expel all traces of carbon dioxide; filter off the sulphur which separates; add a slight excess of ammonia to the boiling solution,[3] when a lemon-yellow voluminous precipitate of ammonium uranate—$(NH_4)_2U_2O_7.nH_2O$—separates. The precipitate rapidly becomes less bulky, darker in colour, and more easy to filter and wash; but at best, the precipitate filters with difficulty. Wash the precipitate with a 2 per cent. solution of ammonium nitrate,[4] *i.e.* 2 grms. of salt in 100 c.c. of water.

When the precipitation is made with ammonia in the presence of alkalies or alkaline earths, the ammonium uranate is sure to be contaminated with these bases.[5] Hillebrand found that, when precipitated from hot solutions in the presence of ammonium chloride, the ammonium uranate was practically free from alkalies when the precipitation was repeated twice; and after three precipitations the uranate was practically pure.

The precipitate is ignited in a porcelain or platinum crucible with the filter paper, slowly at first so as to burn the paper, then 15 minutes in the blast, and finally, let the precipitate cool slowly in a gradually decreasing flame. The crucible is kept in a slanting position to ensure a free circulation of air. The crucible is finally cooled in the desiccator, and weighed as the dark green or velvety black powder of the oxide—U_3O_8.[1] The filtrates contain lime, magnesia alkalies, and possibly some of the rare earths.

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[1] The calcium oxide so obtained is added to that obtained in the previous precipitation.

[2] The uranium oxide finally obtained is not perfectly free from the rare earths, and, in the analysis of some uranium minerals, Hillebrand (*l.c.*) recovered the uranium oxide—amounting to a quarter or a third per cent. of the whole material—by treating the dried nitrates with ether; filtering; washing with ether; dissolving the nitrates of the earths containing some uranium in water acidulated with a drop of nitric acid; adding oxalic acid to the hot solution; after evaporating to dryness. The earths were added to the main portion. A second precipitation by ether will ensure the removal of the last traces of the earths from the uranium.

[3] The ammonia should be free from carbonates. If carbonates be present, the precipitation will be incomplete. Ammonium sulphide may also be employed in place of ammonia. Ammonium uranate is soluble in alkaline carbonates, and also slightly soluble in water; but it is not soluble in water containing ammonia, ammonium nitrate, or ammonium chloride. The presence of tartaric acid, oxalic acid, and many other non-volatile organic acids prevents the precipitation—R. Fresenius. If iron be separated from uranium by ammonium carbonate, the iron is free from uranium, but the uranium contains iron—the iron can, however, be removed by fusing the precipitate with potassium bisulphate, dissolving in water, filtering, neutralising the filtrate, and precipitating the iron with ammonium sulphide—F. Glaser, *Chem. Ztg.*, **36.** 1166, 1912.

[4] E. F. Kern (*Journ. Amer. Chem. Soc.*, **23.** 685, 1901) obtained the same results by igniting with or without the filter paper.

[5] R. Fresenius, *Quantitative Chemical Analysis*, London, **1.** 533, 1876; W. F. Hillebrand, *Amer. J. Science* (4), **10.** 136, 1900.

§ 258. The Gravimetric Determination of Uranium as Uranium Phosphate.

Owing to the difficulty in obtaining an oxide of constant composition when ammonium uranate is ignited, many prefer to precipitate the uranium as phosphate.[2] The old objection that the precipitate is too slimy to filter and wash with comfort, does not apply if the precipitation be made as described below. Dissolve the oxide in dilute nitric acid.[3] Add ammonia until a precipitate just begins to form. Add just the right amount of nitric acid to clear the solution, and then 2–3 grms. of microcosmic salt,[4] dissolved in a little water, together with 10 grms. of crystalline sodium thiosulphate.[5] The solution becomes yellow, and deposits a voluminous precipitate. Boil about 15 minutes. The precipitate then coagulates and settles rapidly. The precipitate is readily washed by decantation with water containing a little ammonium nitrate.[6] Transfer the precipitate to a Gooch's crucible containing ignited asbestos, wash, and dry. Ignite the precipitate at a red heat for 10 to 20 minutes. If the precipitate be greenish coloured,[7] add a few drops of nitric acid (say, sp. gr. 1·42), dry over the flame, and re-ignite at low redness over a Bunsen's burner. The lemon-yellow compound $(UO_2)_2P_2O_7$ is formed on ignition. Multiply its weight by 1·29 to get the equivalent amount of U_3O_8. The precipitate is somewhat hygroscopic, and should not therefore be needlessly exposed to the air before weighing.

In illustration of the results which can be obtained by precipitating uranium nitrate solutions, containing the equivalent of 0·1925 grm. of uranium, with microcosmic salt, Kern gives:

0·1921; 0·1927; 0·1925; 0·1905; 0·1903; 0·1921; 0·1918.

§ 259. The Separation of Uranium as Uranium Ferrocyanide—Fresenius and Hintz's Process.

It is difficult to separate the members of the hydrogen sulphide group from uranium, since the precipitate—arsenic and copper sulphides—must be dissolved and reprecipitated a number of times to eliminate the uranium. Phosphoric acid too prevents clean separations of iron and uranium.

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[1] This usually contains some patches of a yellowish-brown colour. C. Zimmermann (*Liebig's Ann.*, **232**. 273, 1886) says that the theoretical U_3O_8 is only formed if the calcination be done in a current of oxygen, and W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, **78**. 53, 1891) confirms this. However, E. F. Kern (*l.c.*) considers that the oxide is sufficiently near U_3O_8 for all practical requirements, when the ignition is performed as described in the text. Kern also tried igniting the ammonium uranate in a current of hydrogen and weighing as UO_2, but the results were not so satisfactory as when the precipitate was weighed as U_3O_8.

[2] C. Leconte, *Pharm Journ.*, **13**. 80, 1854; F. Pisani, *Chem. News*, **3**. 211, 1862; *Compt. Rend.*, **52**. 106, 1861.

[3] Sulphuric acid is used if the precipitate is to be evaluated volumetrically as described later.

[4] That is, about ten times the amount actually required to precipitate the uranium.

[5] In the event of lime and magnesia being present, acidify the solution with acetic acid; add 5 c.c. of concentrated ammonium acetate to prevent the precipitation of calcium phosphate. Lime is determined in the filtrate by neutralising most, but not all, of the free acetic acid, and precipitation as oxalate and estimation as sulphate (H. Brearley, *The Analytical Chemistry of Uranium*, London, 24, 1903). The magnesia is determined in the filtrate as usual.

[6] Test the filtrate for uranium with potassium ferrocyanide.

[7] This is always the case if the ignition temperature be rather high. The green precipitate is generally supposed to be $U_2O_3 . P_2O_7$.

In this special case, Fresenius and Hintz[1] add an excess of potassium ferrocyanide to the slightly acid filtrate from the silica, and saturate the liquid with sodium chloride to facilitate the flocculation of the precipitated uranium, copper, and iron ferrocyanides. Otherwise the precipitate is exceedingly difficult to filter and wash. Wash the precipitate by decantation, and afterwards on a filter paper with a solution of sodium chloride. Digest the precipitate in the cold with dilute potassium hydroxide, and when the transformation of the ferrocyanides to hydroxides is complete, decant the liquid, wash the precipitate with water containing ammonium chloride and ammonia until ferrocyanide can no longer be detected in the acidulated filtrate. Dissolve the precipitate in hydrochloric acid[2] and, if necessary, concentrate the solution by evaporation. Neutralise the greater part of the acid with ammonia; add ammonium carbonate to the clear liquid; filter and wash the ferric hydroxide with water containing a little of the filtrate. Heat the filtrate to expel most of the ammonium carbonate, acidify with hydrochloric acid, and boil the solution so as to dissolve the yellow flocculent precipitate. Remove copper from the solution by passing hydrogen sulphide through the hot liquid. The uranium can be determined in the filtrate as usual—page 490 or 491.

§ 260. Belohoubek's Volumetric Process for Uranium.

In 1867, Belohoubek[3] devised a method for the volumetric determination of uranium based on the reduction of uranium salts to uranous—UO_2—salts by means of zinc in acid solutions, precisely in the same way that ferric salts are reduced, and, as with iron, the subsequent titration with permanganate to re-oxidise the uranous salts. The reducing action is represented:

$$UO_2SO_4 + Zn + 2H_2SO_4 = ZnSO_4 + U(SO_4)_2 + 2H_2O.$$

There is not a general agreement as to the accuracy of the results. Some consider that zinc reduces further than the UO_2 stage, and that the reduced solution must be exposed to the air to re-oxidise it to UO_2 before the permanganate titration is made.[4] Kern, however, has shown that the reduction does not proceed beyond the UO_2 stage when sulphuric acid is used, even upon five hours' boiling.[5]

The washed precipitate of, say, uranous ammonium phosphate is dissolved in sulphuric acid, and the uranyl sulphate UO_2SO_4 reduced with zinc, magnesium, or aluminium[6] to uranous sulphate in an excess of sulphuric acid. According to

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[1] R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **34**. 437, 1895; *Chem. News*, **72**. 206, 1895.

[2] If any ferrocyanide remains undissolved, repeat the treatment.

[3] A. Belohoubek, *Journ. prakt. Chem.* (1), **99**. 231, 1867; *Zeit. anal. Chem.*, **6**. 120, 1867; O. Follenius, *ib.*, **11**. 179, 1872; C. Zimmermann, *Liebig's Ann.*, **213**. 285, 1882; F. Ibbotson and S. G. Clarke, *Chem. News*, **103**. 146, 1911; E. de M. Campbell and C. E. Griffin, *Journ. Ind. Eng. Chem.*, **1**. 455, 1910.

[4] O. S. Pullman, *Amer. J. Science* (4), **16**. 229, 1903; H. M. Goettsch, *Journ. Amer. Chem. Soc.*, **28**. 1541, 1906; H. N. M'Coy and H. H. Bunzel, *ib.*, **31**. 367, 1909.

[5] E. F. Kern, *Journ. Amer. Chem. Soc.*, **23**. 685, 1901; *Chem. News*, **84**. 224, 236, 250, 260, 271, 283, 1901; E. de M. Campbell and C. E. Griffin, *ib.*, **101**. 7, 1910; *Journ. Ind. Eng. Chem.*, **1**. 661, 1909.

[6] According to Kern (*l.c.*), uranyl salts are not reduced by hydrogen sulphide. Hence, there is a probability that iron and uranium could be determined in one solution by consecutive reductions with hydrogen sulphide and zinc. The results with zinc, magnesium, and aluminium are the same. Magnesium reduces fastest, zinc slowest. The reductor also gives satisfactory results. Kern did not get satisfactory results with stannous salts. Hydrochloric acid is also objectionable. Nitric acid must, of course, be absent.

Kern, the ratio of the volume of free sulphuric acid to the total volume of the solution should not be less than 1 : 5, nor more than 1 : 6. During the reduction, the colour of the solution passes from yellow to light green, and finally to a green tinged with blue. This colour is retained even when the reduction has been in progress for four hours. Owing to the fact that there is no satisfactory test to determine whether all the uranyl sulphate has been reduced, it is best to let the reduction proceed for about an hour.[1] Then dilute the solution with recently boiled distilled water until it is almost colourless, and then titrate with N-potassium permanganate[2] until a permanent pink blush remains suffused through the solution. The oxidation by the permanganate is represented by the equation:

$$5U(SO_4)_2 + 2KMnO_4 + 2H_2SO_4 + 2H_2O \rightarrow 5UO_2SO_4 + 2MnSO_4 + 2KHSO_4 + 3H_2SO_4.$$

In illustration of the results obtained with solutions of known strength, with zinc reduction, the following numbers might be quoted:[3]

Used . . .	0·15406	0·15464	0·09643	0·19286	0·23050	grm.
Found . . .	0·15400	0·15400	0·09625	0·19250	0·23100	grm.

Volumetric Determination of Uranium and Vanadium.—Sulphur dioxide does not reduce uranyl solutions. Hence, vanadium can be determined volumetrically in presence of uranyl salts. Griffin[4] tried to determine one in presence of the other by first reducing with sulphur dioxide, and titration with permanganate; and then reducing both by zinc, and titrating. By subtraction, the amount of permanganate required for the oxidation of each can be readily found. Difficulties were encountered owing to the fact that, while zinc reduces the vanadic salts, V_2O_5, to vanadous salts, V_2O_2, the latter is practically oxidised by air before one can titrate, no matter how rapidly the work is done. Reduction in the reductor, fig. 104, page 191, gave good results, but even then an atmosphere of carbon dioxide above the liquid in the flask is needed for good results. The method is otherwise similar in principle to those indicated on page 482 for vanadium and iron, and for vanadium and molybdenum.[5]

Evaluation of Commercial Salts.—Sodium uranate and uranium oxides, soluble in sulphuric acid, can be treated in a similar manner. There is a difficulty in dissolving the oxide U_3O_8. It dissolves very slowly in sulphuric acid. In that case, a little nitric acid, say 20 c.c. of concentrated acid, facilitates the dissolution. The solution must then be boiled to drive off the nitric acid, before the permanganate titration, etc.[6]

Hillebrand[7] effects solution by heating, say, 0·2 grm. of the oxide in 10 to 15 c.c. of sulphuric acid (free from nitric acid), at 150° to 175°, in a sealed glass tube. The dry powder is placed in a thick glass tube, sealed at one end, and the sulphuric acid (water 6, acid 1) added through a long-necked funnel in such a way as to keep the open end of the tube dry. When the carbon dioxide has had sufficient time to escape, draw out the open end in the blast blowpipe to a capillary point, and seal off the end. After the digestion in a suitable furnace so that there is no risk if the tube bursts, let the tube cool, open by scratching the capillary end with a file and applying a hot glass rod. Wash the contents of the tube into a beaker, reduce with zinc, and titrate with permanganate as described above.[1]

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[1] Kern says that 1 hr. is sufficient for 0·1 grm. of uranium, $1\frac{1}{2}$ hr. for 0·2 grm. uranium.

[2] According to C. E. Griffin (*Min. Eng. World*, **37**. 247, 1912), permanganate solutions not exceeding $\frac{1}{20}$N in strength give a sharper end point than more concentrated solutions.

[3] For interference with iron and titanium salts, see V. Auger, *Compt. Rend.*, **155**. 647, 1912. In this case, add a large excess of sodium tartrate and reduce with titanous chloride, using nitro-induline as indicator; then titrate the uranium with a ferric salt in acid solution, using potassium thiocyanate as indicator.

[4] C. E. Griffin, *Min. Eng. World*, **37**. 247, 1912.

[5] If uranium and vanadium occur together, A. N. Finn (*Journ. Amer. Chem. Soc.*, **28**. 1443, 1906) proceeds as follows:—Take up the sodium carbonate fusion with water, and treat the acidified solution with sodium carbonate. The filtrate contains uranium, vanadium, etc. Make the solution alkaline with ammonia, and precipitate the uranium as phosphate (page 490). The filtrate contains the vanadium, the precipitate the uranium. Dissolve the latter in sulphuric acid and determine the uranium by the volumetric process (page 491); the vanadium in the filtrate is acidified with sulphuric acid, reduced with sulphurous acid, etc., as described page 480.

[6] For the rate of oxidation of uranous solutions, see H. N. M'Coy and H. N. Bunzel, *Journ. Amer. Chem. Soc.*, **31**. 367, 1909. [7] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **78**. 90, 1889.

§ 261. Operations with Sealed Tubes.

Closing One End.—A piece of glass tubing—between 35 and 40 cm. long and 16–17 mm. internal diameter, with walls over 3 mm. thick—is carefully sealed at one end so that the glass is not thickened into a blob. If a blob does form, it can generally be removed by alternately heating and blowing. Tubes ready sealed at one end can be purchased from the dealers.

Charging the Tube.—The tube is washed (page 36) and dried. The dry powder under investigation is introduced into the tube so that the powder does not touch the side of the tube near the open end. The necessary acid is added by means of a long-stemmed funnel without wetting the sides of the tube near the open end.

Sealing the Tube.—About 5 cm. of the glass at the open end is very gradually heated by revolving it for several minutes in the smoky flame of a gas blowpipe. The tube is held inclined at an angle of about 45°. The blast is gradually turned on and the tube revolved until the glass begins to soften. One end of a glass rod, about 13 cm. long, is pressed against the edges of the glass tube—*a*, fig. 156. The blowpipe flame is reduced to about 8 or 10 cm. length, and directed at a point about 2 or 3 cm. away from the end to which the glass rod is attached. All the time the tube is being heated, it is slowly revolved so that the glass is heated as uniformly as possible, but not drawn out.[2] The glass begins to thicken, and the inside diameter of the tube contracts (see the photograph, fig. 157). When the inside diameter of this part of the tube has contracted to about 3 mm., the tube is withdrawn from the flame, and the thickened portion is drawn out to form a capillary end—*b*, fig. 156. In a few seconds, when the capillary has cooled until it is rigid, seal the tip as shown at *c*, fig. 156. The tube is allowed to cool, capillary end upwards.

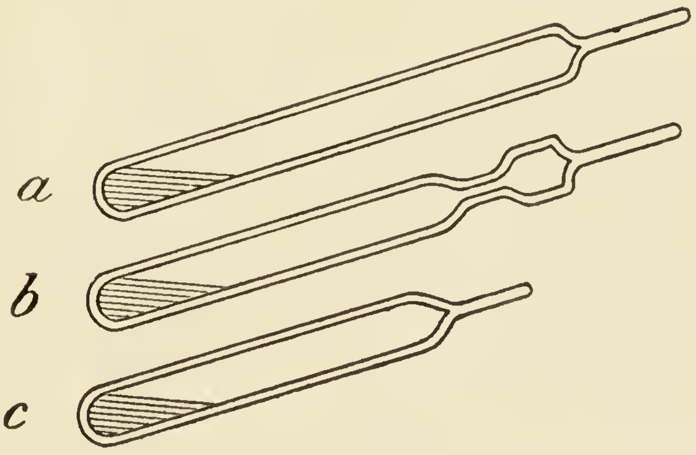

Fig. 156.—Three stages in sealing the tube.

Heating the Sealed Tube.—The sealed tube is then placed in a metal cylinder with a screw cap. The metal cylinder is placed in a cold tube furnace—Meyer's, Gattermann's, Volhard's, Habermann's, etc.[3] The tube furnace is gradually heated to the desired temperature. The furnace is placed so that no damage will be done if the tube bursts. The gas is extinguished when the tube has been heated long enough, and the tube allowed to cool.

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[1] With much stronger acid, Hillebrand obtained green crystals of a complex uranium salt in the sealed tube.

[2] Hard glass tubes are not usually thickened, but drawn out at once into a wide capillary about 1½ cm. long. The flame is directed at the base of this capillary, and the glass gradually drawn out so as to form a capillary 2 or 3 cm. long. This is sealed off at the tip. An oxy-coal gas flame gives the best results with hard glass.

[3] L. Meyer, *Ber.*, **14**. 1087, 1883; J. Volhard, *Liebig's Ann.*, **284**. 233, 1895; J. Habermann, *Zeit. anal. Chem.*, **13**. 165, 1874.

Opening the Sealed Tube.—When cold, withdraw the tube from the iron casing so that the capillary end, and only the capillary end, projects. If the reaction in the tube is such as to develop gas, place the tip of the capillary in the Bunsen's flame so as to drive out the liquid which condenses there. Then heat the tip until the glass softens. The pressure inside the tube blows a vent-hole in the glass. When the pressure is relieved, and *not before*, withdraw the tube from its metal casing, file a mark on the glass tube about 2 cm. below the base of the capillary, and touch the file mark with the red-hot tip of a drawn-out piece of glass tubing. The tube will crack, and the crack is carried round the tube by means of the hot glass tip. The end of the tube is then removed. The tube is kept nearly horizontal during this operation, so as to prevent fragments of glass dropping into the tube. The contents of the tube are then washed into a beaker, and treated as required.

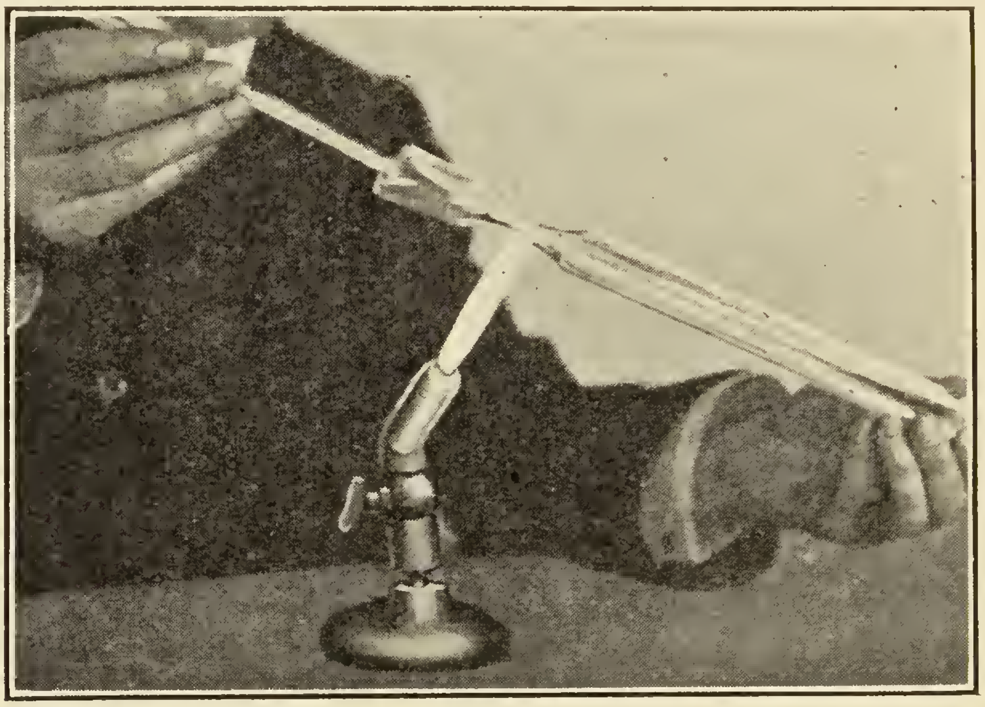

FIG. 157.—Sealing the glass tube.

NOTE FOR PAGE 476.

Valuation of Chrome Iron Ores.—Chrome iron ores are valued on their Cr_2O_3 contents. The market value fluctuates. The unit for high-grade, hand-picked, cobbed ores is 50 per cent. Cr_2O_3, with a premium of, say, 2s. per unit per ton over 50 per cent., and a deduction of, say, 2s. per unit below 48 per cent. Cr_2O_3. Second-grade ores are referred to a 45 per cent. unit, with a premium of, say, 2s. per unit up to 48 per cent. Cr_2O_3. Ores carrying between 40 and 45 per cent. Cr_2O_3 inclusive are third-grade ores. The standard is 40 per cent. Cr_2O_3, and a premium or deduction is allowed for every unit above or below this standard. The so-called "concentrates" are divided into first and second grades; the former are referred to the 50 per cent. unit, and the latter to the 45 per cent. unit, with premiums and deductions as before. Much crude ore is sold for furnace linings for steel furnaces. A minimum of 5 per cent. silica was formerly allowed, but ores with 8 per cent. of silica now find a market in the chromite brick industry.

CHAPTER XXXV.

ZIRCONIUM, THORIUM, AND THE RARE EARTHS.

§ 262. The Separation and Detection of Zirconium.

MINUTE quantities of zirconium occur in many if not most silicates of the type of Cornish stone. Zirconia is also used as a constituent of certain white enamels and opaque glazes, and in special cases as a high temperature refractory material. In the regular course of a silicate analysis, zirconia appears with the ammonia or ammonium sulphide precipitate, and, if ignored, would be reported as alumina. If the zirconia is to be determined, its weight must be deducted from the weight of the alumina as determined by the method of pages 182 and 210.

The Separation of Zirconium and Aluminium from Iron.—The oxides are fused with potassium pyrosulphate, and the resulting cake, when cold, is dissolved in water. The solution is nearly neutralised with sodium carbonate and made up to 300–400 c.c. Then an excess (say 5 grms.) of sodium thiosulphate—$Na_2S_2O_3$—is added and the solution is boiled until the smell of sulphur dioxide is no longer perceptible (one to two hours suffice). The ferric iron, it will be observed, is reduced to the ferrous condition. The precipitation seems to be a result of hydrolysis (pages 181 and 207), and the thiosulphate serves to keep the solution neutral, but does not directly effect the precipitation. The reaction is usually symbolised :

$$2AlCl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3S + 3SO_2.$$

The precipitate may contain sulphur mixed with the hydroxides of aluminium,[1] zirconium, titanium,[2] and thorium, if present.[3] The filtrate contains salts of iron, beryllium, cerium, lanthanium, didymium, etc. The precipitate is washed, dissolved in dilute sulphuric acid, and filtered from the sulphur, if necessary. This method gives good separations of zirconium and aluminium from iron.

The Separation of Zirconium from Aluminium.—Zirconium (with thorium, if present) can be separated from aluminium as a sparingly soluble basic zirconium iodate in neutral or feebly acid solutions.[1] Suppose the solution has the equivalent of 0·1 grm. of zirconium per 100 c.c. in a solution acidified with hydrochloric acid. Add sodium carbonate to the solution until a faint turbidity appears when the solution is thoroughly agitated. Add the smallest amount of dilute hydrochloric acid necessary to just give a clear solution, and then an excess of sodium iodate. Heat the mixture for about 15 minutes, and then let it stand for about 12 hours. Filter off the precipitated iodate, and wash with boiling water. Dissolve it in hydrochloric acid, and precipitate the zirconium hydroxide by the addition of ammonia.[2] The precipitate is washed, etc., as if it were aluminium hydroxide (page 182), and finally weighed as zirconium oxide, ZrO_2. The aluminium in the filtrate from the basic zirconium iodate is determined by the ammonia precipitation in the usual manner.

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[1] Chancel's process for the separation of aluminium from iron (M. F. Chancel, *Compt. Rend.*, **46**. 987, 1858 ; F. Stromeyer, *Liebig's Ann.*, **113**. 127, 1860) ; P. T. Cleve, *Zeit. Kryst.*, **16**. 362, 1890 ; R. Hermann, *Journ. prakt. Chem.* (1), **97**. 330, 1866 ; E. W. Parnell, *Chem. News*, **21**. 54, 1870 ; J. E. Stead, *ib.*, **63**. 11, 172, 1891 ; *Journ. Soc. Chem. Ind.*, 8. 965, 1889 ; A. Carnot, *Chem. News*, **64**. 73, 1891 ; *Compt. Rend.*, **111**. 914, 1890 ; H. Lasne, *ib.*, **121**. 63, 1896 ; *Bull. Soc. Chim.* (3), **15**. 118, 1896 ; E. Donath and R. Jeller, *Rep. anal. Chem.*, **7**. 35, 1887). W. Gibbs (*Zeit. anal. Chem.*, **3**. 389, 1864) and A. Zimmermann (*Ueber die Trennung der Thonerde und der Beryllerde*, Berlin, 1887) have shown that the separation is not complete unless the boiling be very prolonged.

[2] F. Stromeyer (*Liebig's Ann.*, **113**. 127, 1860) separates zirconium and titanium from iron by this process. M. Dittrich and S. Freund, *Zeit. anorg. Chem.*, **56**. 337, 1907 ; R. Hermann, *Journ. prakt. Chem.* (1), **97**. 330, 1866. J. T. Norton (*Amer. J. Science* (4), **12**. 115, 1901 ; *Chem. News*, **84**. 254, 261, 1901) discusses the influence of pressure on precipitations by sodium thiosulphate.

[3] If thorium should be present, it must be separated by the oxalic process described later.

The Separation of Zirconium from Titanium, Aluminium, and Iron.[3]—There is no particular difficulty in separating zirconium in the absence of titanium, nor in separating titanium in the absence of zirconium, but together the individuality of the elements, as Crookes[4] expresses it, is destroyed. The reactions these elements undergo when they occur alone do not necessarily occur when the two elements are mixed together. For instance, titanium hydroxide is completely precipitated when a dilute solution of titanium sulphate is boiled for some time; but if zirconium be present, there may be either an incomplete precipitation or none at all. The phenomenon is by no means uncommon: aluminium hydroxide, for example, is dissolved by ammonium carbonate solutions in appreciable quantities when beryllium hydroxide is present, but alone, the alumina is scarcely affected.[5] A similar observation was made respecting niobium and titanium on page 420.

A fairly concentrated solution of hydrogen peroxide (say, 30 per cent., or a "100 vol." solution) gives no precipitate with a solution of zirconium nitrate or oxychloride neutral or acidified with sulphuric acid. On the other hand, a white, flocculent precipitate is obtained with solutions of zirconium sulphate. The precipitate is said to be a hydrated peroxide—$Zr_2O_5 . 4H_2O$. If the solution be agitated and warmed, and the hydrogen peroxide is present in great excess, the reaction is quantitative; but if the hydrogen peroxide be in dilute solution, the separation is very slow. The separation is best performed in a feebly acid solution, for if too much acid be present, no precipitation occurs. The exact proportions have not been worked out, but the precipitate is practically insoluble in 1 per cent. solutions of sulphuric acid.[6]

Bailey considers that this reaction furnishes a convenient means of separating zirconium from titanium, iron, aluminium, niobium, tantalum, thorium, yttrium, cerium, etc. The method gives good results only under very special conditions, and it is accordingly rarely used. When sodium phosphate—Na_2HPO_4—is also added to the solution just after the addition of the hydrogen peroxide, Hillebrand has shown that a white, slimy, voluminous precipitate of zirconium phosphate—possibly $Zr_5H_4(PO_4)_8 . 6H_2O$—separates. The precipitate is not soluble in water, but it is readily soluble in dilute acids. The precipitate can be purified from titanium and rare earths by pouring dilute hydrofluoric acid (1 : 5) several times through the filter paper supported in a celluloid or rubber funnel, and collecting the runnings in a platinum dish. The rare earth phosphates are not soluble in hydrofluoric acid. Evaporate the solution with a few drops of sulphuric acid, and, when the hydrofluoric acid is expelled, repeat the operation with hydrogen peroxide and sodium phosphate.

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[1] J. T. Davis, *Journ. Amer. Chem. Soc.*, **11**. 26, 1889; R. J. Meyer and M. Speter, *Chem. Ztg.*, **34**. 306, 1910; R. J. Meyer, *Zeit. anorg. Chem.*, **71**. 65, 1911. Cerium and yttrium iodates are not very soluble in water, but they are readily soluble in nitric acid. Zirconium and thorium iodates are not soluble in nitric acid provided an excess of alkaline iodate be present. Accordingly, thorium, the rare earths, titanium, and iron may give precipitates in feebly acid solutions.

[2] There is too much risk of loss by decrepitation to render it safe to calcine the iodate.

[3] M. Dittrich and R. Pohl (*Zeit. anorg. Chem.*, **43**. 236, 1905) precipitate the titanium and zirconium hydroxides; wash, etc., and weigh. The titanium is determined colorimetrically, and the zirconium by difference.

[4] W. Crookes, *Select Methods in Chemical Analysis*, London, 139, 1905.

[5] C. A. Joy, *Amer. J. Science* (2), **36**. 83, 1863; *Chem. News*, **8**. 183, 197, 1863.

[6] Hydrochloric acid dissolves the precipitate with the liberation of chlorine. See W. Biltz and W. Mecklenburg, *Zeit. angew. Chem.*, **25**. 2110, 1912.

The Turmeric Test for Zirconium.—Dissolve the purified zirconium phosphate in a little dilute hydrofluoric acid (1 : 5), evaporate the solution almost to dryness, and dip a piece of turmeric paper into it. Dry the paper in a test tube in a steam oven (about 100°). A pink coloration represents zirconium. The presence of 0·0001 grm. of zirconium is nearly the limit of the test.[1] Titanium gives a similar coloration, and it is even more sensitive than zirconium. Greater quantities of titanium give a brown coloration,[2] but not if the titanium be first reduced to titanium oxide[3] by means of zinc in an acid solution. In the latter case, the titanium may be oxidised as the paper dries, and so develop the titanic acid coloration. Blank tests with hydrofluoric acid are not always satisfactory, and the turmeric test is not therefore very reliable except under favourable conditions.

§ 263. The Gravimetric Determination of Zirconium as Phosphate.

Decomposition of the Silicate.—Two grams of the dry powder are fused with from 12 to 15 grms. of sodium carbonate.[4] Digest the cold mass with water. When the fused cake is quite disintegrated, add a drop or two of alcohol or hydrogen peroxide to reduce the sodium manganate. Wash the disintegrated residue with a 2 per cent. solution of sodium carbonate.[5] The filtrate contains chlorine, fluorine, sulphur, silica, alumina, etc.[6] The residue on the filter paper is washed into a beaker by projecting a strong jet of warm (70°) dilute sulphuric acid (1 : 20)[7] against all parts of the filter paper. About 50 c.c. of the acidulated water should suffice. Add two or three drops of sulphurous acid to dissolve any brown manganese hydroxide which may be present. Warm the solution to about 70°. When all effervescence has ceased, add a few drops more of the acidulated water to make sure that all action is over.[1] The liquid should be distinctly acid.[2] Filter the liquid into an Erlenmeyer's flask (150 c.c.),[3] and wash with warm (70°) acidulated water. The filtrate contains the iron, aluminium, and most of the zirconium. Some zirconium remains in the residue along with the silica and any barium sulphate which might be present. To recover this zirconium, ignite the filter paper and contents in a platinum crucible, and treat the mass with hydrofluoric and sulphuric acids in order to expel the silica, which holds back some of the zirconium very tenaciously. Take up the residue with hot dilute sulphuric acid (1 : 20). Barium sulphate remains insoluble (page 618). The filtrate contains titanium, aluminium, iron, zirconium, rare earths, etc. Combine the two filtrates. Precipitate the zirconium by the hydrogen peroxide and sodium phosphate process described below. The sequence of the operations employed for separating the zirconium from an insoluble silicate is therefore represented by the scheme :

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[1] B. E. Schlesinger, *A Systematic Procedure for the Qualitative Detection of the Rare Metals of Certain Groups*, Boston, Mass., 1902 ; C. R. Böhm, *Die Darstellung der seltenen Erden*, Leipzig, 1905 ; P. E. Browning, *Introduction to the Rarer Elements*, New York, 1908 ; J. Ohly, *Analysis, Detection, and Commercial Value of the Rare Metals*, Denver, 1903 ; P. Truchot, *Les Terres Rares*, Paris, 1898 ; J. Herzfeld and O. Korn, *Chemie der selten Erden*, Berlin, 1901 ; J. von Panayeff, *Verhalten der Wichtigsten seltenen Erden zu Reagentien*, Halle a. S., 1909 ; R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden und Erdsäuren*, Stuttgart, 1912 ; W. Crookes, *Select Methods in Chemical Analysis*, London, 1905.

[2] Boric, niobic, tantalic, and molybdic oxides also give the brown coloration with turmeric paper. The paper reddened with boric acid becomes blue when touched with a dilute solution of potash, while the reddening with zirconia is only affected in the ordinary manner. K. Kraut, *Zeit. anal. Chem.*, **4**. 168, 1865 ; A. Müller, *Journ. prakt. Chem.* (1), **80**. 118, 1860.

[3] F. Pisani, *Compt. Rend.*, **59**. 301, 1864 ; *Chem. News*, **10**. 218, 1864.

[4] If sulphur is to be determined, add between 1 and 2 grms. of sodium nitrite and note the precautions stated on page 617.

[5] If water be employed, the later washings sometimes run through turbid. The sodium carbonate should be free from bicarbonate.

[6] If desired, the filtrate can be made up to, say, 150 c.c., and equal portions taken for the determination of fluorine, sulphur, and chlorine. But 50 c.c., that is, one-third of 2 grms., may not contain enough for a determination of each of these materials.

[7] M. Wunder and B. Jeannerct (*Zeit. angew. Chem.*, **50**. 733, 1911) remove the iron from the residue by extraction with hot hydrochloric acid (1 : 1) ; but L. Weiss and W. Trautmann (*Zeit. anal. Chem.*, **51**. 303, 1912) say that the sodium zirconate, Na_2ZrO_3, is appreciably soluble in this liquid.

$$\begin{array}{l}\text{Sod. carb}\\\text{fusion.}\end{array}\left\{\begin{array}{l}\text{Soluble in water}\ \ldots\ldots\ \textbf{Chlorine, sulphur, etc.}\\ \text{Insoluble}\left\{\begin{array}{l}\text{Soluble } H_2SO_4\left\{\begin{array}{l}\text{Soluble } Na_2HPO_4\ \ldots\ \textbf{Titanium, etc.}\\ \text{Insoluble } Na_2HPO_4\ \ldots\ \textbf{Zirconium.}\end{array}\right.\\ \text{Insoluble in } H_2SO_4\ \ldots\ldots\ \textbf{Barium, etc.}\end{array}\right.\end{array}\right.$$

Precipitation of Zirconium Phosphate.[4]—Add sufficient (say, 5 c.c.) of a concentrated solution of hydrogen peroxide to the filtrate to maintain a permanent yellow coloration. The object of the hydrogen peroxide is to keep the titanium[5] in solution; and the acidity prevents the precipitation of the aluminium, iron, etc. Add about 1 c.c. of a saturated solution of sodium phosphate—Na_2HPO_4. Fill the flask nearly up to the neck with water, and set it aside in a cool place for a couple of days. If the yellow colour at any time fades away, add more hydrogen peroxide. Gelatinous zirconium phosphate is precipitated. Filter through, say, a 7-cm. filter paper, and wash with water containing a few drops of dilute sulphuric acid. A little titanium phosphate and rare earth phosphates may be carried down with the precipitate. In the former case, the precipitate will probably have a yellow tint. The filtrate is reserved for the determination of the rare earths (page 502).

Purification of the Zirconium Phosphate.—Ignite the precipitate and filter paper in a platinum crucible; fuse with a little sodium carbonate; extract the cold mass with water; filter, wash as before, ignite the filter paper and precipitate; fuse with a little potassium pyrosulphate; dissolve the cold mass in hot water; acidify the solution with a couple of drops of sulphuric acid; and repeat the treatment with hydrogen peroxide and sodium phosphate. Weigh the ignited precipitate as $Na_2O.4ZrO_2.3P_2O_5$. Hence, multiply the weight of the precipitate by 0·5, or more strictly by 0·5014, to get the corresponding amount of zirconia—ZrO_2.[6] The weight of the zirconia, if appreciable, is to be deducted from the collected ammonia precipitate (page 210).

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[1] If the digestion be protracted, gelatinous silica may separate and give trouble in the subsequent filtration.

[2] An excess of sulphuric acid hinders the precipitation of the zirconium phosphate later on, and retards filtration by closing the pores of the filter paper. Not more than 1 per cent. of free H_2SO_4 should be present in the solution.

[3] Filter through the paper used in the previous filtration.

[4] G. H. Bailey, *Journ. Chem. Soc.*, 49. 149, 481, 1886 ; *Chem. News*, 53. 55, 260, 287; 1886 ; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 176. 75, 1900 ; M. Dittrich and R. Pohl, *Zeit. anorg. Chem.*, 43. 236, 1905 ; E. Wedekind, *ib.*, 33. 83, 1903 ; H. Geisow and P. Horkheimer, *ib.*, 32. 374, 1892.

[5] Otherwise titanium phosphate—$Ti(OH)PO_4.H_2O$—would be precipitated—V. Merz, *Journ. prakt. Chem.* (1), 99. 157, 1856.

[6] It is always well to make certain that the precipitate is really zirconia by fusing the mass with a little sodium carbonate. Take up the cold cake with hydrochloric acid ; evaporate the solution until it is nearly dry, and apply the turmeric paper test (page 497). A little thorium, if present in the sample, may even yet be found with the zirconia.

§ 264. The Analysis of Zircon.

Opening up the Mineral.—Fuse a gram of the finely powdered and dried (110°) mineral with 4–5 grms. of sodium bisulphate.[1] The mineral dissolves with great difficulty, and it is necessary to keep it in a molten condition for some time.[2]

Determination of Silica.—When cold, the mass is digested with water. The white insoluble silica is filtered off, ignited, and weighed. Drive off the silica from the ignited mass by treatment with hydrofluoric and sulphuric acid in the usual manner (page 169). This gives the "first silica." Fuse the residue with a little sodium bisulphate, and add the aqueous solution of the fused mass to the main solution.

Hydrogen sulphide is passed through the combined solutions to remove any platinum derived from the crucible. The filtrate is evaporated twice to dryness, with an intervening filtration for silica (page 167). The silica is removed by treatment with hydrofluoric acid. This gives the "second silica." The weight of silica so obtained is added to the previous result. The residue is fused with a little sodium bisulphate and added to the main solution.

Determination of Iron and Alumina.—The solution is approximately neutralised with ammonia, and mixed with sufficient ammonium oxalate and tartrate to prevent the precipitation of aluminium, etc., with ammonia. Add ammonium sulphide to the warm solution (page 208). Keep the solution warm for about an hour.[3] Practically all the iron and a little alumina are precipitated. These may be determined in the usual manner.[4]

Determination of Zirconia.—Evaporate the filtrate from the iron sulphide to dryness in a platinum dish, and ignite the residue until it is almost white. The combustion of the carbon can be facilitated by repeatedly moistening the residue with ammonium nitrate and repeating the ignition. Fuse the white residue with sodium bisulphate. Dissolve the cold mass in water. Add a concentrated solution of hydrogen peroxide (page 496), and follow on with an aqueous solution of sodium hydroxide, added drop by drop, with constant agitation. Zirconium hydroxide separates; the pertitanic acid remains in solution.[1] Dissolve the precipitate in hydrochloric acid; add ammonia; boil off the excess of ammonia; filter; wash; ignite; and weigh as ZrO_2.

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[1] J. M. Matthews, *Journ. Amer. Chem. Soc.*, **20**. 815, 1898. The opening up of zircon is very difficult. Alkaline carbonates, recommended by F. Wöhler (*Liebig's Ann.*, **31**. 122, 1839), P. Berthier (*Ann. Chim. Phys.* (1), **50**. 362, 1832), W. Henneberg (*Journ. prakt. Chem.* (1), **38**. 508, 1846), H. L. Wells and H. W. Foote (*Zeit. anorg. Chem.*, **10**. 434, 1895), L. M. Dennis and A. E. Spencer (*Journ. Amer. Chem. Soc.*, **18**. 673, 1896), and C. F. Chandler (*Pogg. Ann.*, **102**. 446, 1857), act very slowly (T. Scheerer, *ib.*, **59**. 481, 1843). Alkaline hydroxides—with or without alkaline fluorides—are better—E. Linnemann, *Monats. Chem.*, **6**. 335, 1885; *Chem. News*, **52**. 233, 240, 1885; G. H. Bailey, *ib.*, **53**. 55, 260, 287, 1886; **60**. 6, 17, 32, 1889; F. P. Venable, *Journ. Amer. Chem. Soc.*, **16**. 469, 1894; F. P. Venable and W. Belden, *ib.*, **20**. 273, 1898; F. P. Venable and T. Clarke, *ib.*, **18**. 434, 1896; *Chem. News*, **74**. 44, 1896; C. Marignac, *Ann. Chim. Phys.* (3), **60**. 260, 1860; F. Dubois and A. A. da Silveira, *ib.* (1), **14**. 111, 1820; J. J. Berzelius, *Pogg. Ann.*, **4**. 117, 1825; M. Melliss, *Bull. Soc. Chim.* (2), **14**. 204, 1870; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, **1**. 203, 227, 1795. For the method indicated in the text see L. Weiss and R. Lehmann, *Zeit. anorg. Chem.*, **65**. 178, 1910; M. Tcharviani and M. Wunder, *Ann. Chim. Anal.*, **16**. 1, 1911; M. Wunder and B. Jeanneret, *Zeit. anal. Chem.*, **50**. 733, 1911.

[2] For the method of conducting bisulphate fusions, see page 185.

[3] The iron sulphide which first separates is very finely divided, and inclined to pass through the filter paper. The precipitate coagulates and filters easily after standing for an hour.

[4] When the amount of iron is great in comparison with the alumina, a relatively large proportion of the total alumina, according to L. Weiss and R. Lehmann (*Zeit. anorg. Chem.*, **65**. 178, 1909), is precipitated with the iron. If much alumina and little iron be present, most of the alumina will remain in solution. The zircon may have so little alumina that the determination of the alumina with the iron will be sufficiently exact for technical purposes. In that event, the alumina in the analysis will be a little low, and the zirconia a little high, in consequence of the alumina which escapes precipitation with the iron.

The zirconia so obtained is generally contaminated with both silica and alumina. The former is removed by digesting the mass with hydrofluoric and sulphuric acids[2] and repeated calcination with ammonium carbonate in order to remove the fluorine.[3] The zirconia is now contaminated with alumina. For the separation of zirconium and aluminium oxides, see page 495.

Determination of Titanium.—The excess of hydrogen peroxide is decomposed by boiling the filtrate. Take care to avoid loss by spurting owing to the decomposition of the hydrogen peroxide. Precipitate the titanium by the addition of ammonia, or apply the colorimetric process.[4]

§ 265. The Rare Earths.

The term "rare earth" is applied to certain trivalent metallic oxides—yttria and ceria earths—which were formerly regarded as elementary bodies. They fall into the same analytical group as aluminium, iron, beryllium, etc., from which they can be separated as oxalates insoluble in dilute acids, and in cold ammonium oxalate solutions. The solubilities of the oxalates[5] of some of these earths in water, in solutions of ammonium oxalate, and in sulphuric acid solutions are shown in the following table:—

Table LXII.—Solubilities of the Rare Earth Oxalates.

Oxalate.	Water. Grm. per litre.	Ammonium oxalate. One gram of oxalate in 38 grms. of water dissolves grm.	Normal sulphuric acid. Grms. of anhydrous oxalate per litre.
Lanthanum	0·00062	0·00023	2·56
Praseodidymium	0·00074	0·00026	1·23
Neodidymium	0·00049	0·00034	1·00
Cerium	0·00041	0·00042	1·64
Yttrium	0·00100	0·00256	...
Ytterbium	0·00334	0·02437	...
Thorium	...	0·62000	0·190

There are some doubts about the identity of many of the rare earths, and the individuality of some has not yet been satisfactorily demonstrated. The following are the more important types:—

1. YTTRIUM EARTHS—*e.g.*, yttria, erbia, terbia, holmia, thulia, dysprosia, ytterbia (neoytterbia), lutecia, europia, etc.

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[1] A. Classen, *Ber.*, 21. 370, 1888.

[2] Zirconium may be volatilised when the silica is removed by treatment with hydrofluoric acid, unless, say, the mass is mixed with 20 times its bulk of sulphuric acid and 45 times its volume of hydrofluoric acid. The zirconia is finally weighed as oxide, ZrO_2. E. Wedekind, *Ber.*, 44. 1753, 1911.

[3] This gives the "third silica," which, added to the "first" and "second" silica, gives the "total silica."

[4] The lime and magnesia are determined as indicated on pages 213 and 218, and the alkalies by J. L. Smith's process (page 222). For traces of niobium, vanadium, and the rare earth elements, see the index.

[5] E. Rimbach and A. Schubert, *Zeit. phys. Chem.*, 67. 183, 1909; B. Brauner, *Journ. Chem. Soc.*, 73. 951, 1898.

2. CERIUM EARTHS—*e.g.*, ceria, lanthana, neodidymia, praseodidymia, samaria, scandia, decipia, gadolinia, etc.

Thorium and zirconium earths are not included in the above definition of the rare earths, but in general analytical work it is often convenient to include both thoria and zirconia with the rare earths, because they all have many analogous properties.

The Separation of Thoria, Ceria, and the Yttria Earths from the Ammonia Precipitate.—In determining the rare earths, it is often convenient to dissolve the ammonia precipitate containing the aluminium, iron, yttrium, cerium, thorium, zirconium, uranium, etc., hydroxides or phosphates in the smallest possible quantity of hydrochloric acid; and treat the solution with oxalic acid. The yttrium, cerium, and thorium oxalates are precipitated, while zirconium, aluminium, iron, and uranium[1] remain in solution.[2] The latter can be separated by processes previously described. The chief source of difficulty is the fact that the acidity of the solution requires careful adjustment, or appreciable quantities of the cerium, yttrium, and thorium oxalates will pass into solution, or else the precipitate may be contaminated with zirconium oxalate. The conditions for successful work with ceria[3] have been investigated, but not for yttria.[4] The best results are obtained when the ammonia precipitate is dissolved in $\frac{1}{4}$N- to $\frac{1}{2}$N-hydrochloric acid—about 50 c.c. of acid are required per gram of the earths. Add 40–50 c.c. of a 10 per cent. solution of oxalic acid, and keep the solution at about 60° for about 12 hours. The precipitate is washed with warm water. The precipitate can be calcined to convert the oxalates into oxides, and weighed.

If it be desired to separate the thoria, yttria, and ceria, the washed precipitate is digested on a water bath with concentrated nitric acid (sp. gr. 1·4) and one drop of $\frac{1}{10}$N-potassium permanganate, which accelerates the rate of dissolution by the nitric acid. The dish should be covered with a clock-glass to prevent loss by spurting. The oxalates will be decomposed in a short time. The excess of acid is removed by evaporation, and the thorium precipitated by the hydrogen peroxide process (page 505), or by the sodium thiosulphate process.

Separation of Thorium by Sodium Thiosulphate.—The nitrate solution is repeatedly evaporated with hydrochloric acid to convert the nitrates into chlorides (page 427). Dilute the solution and heat it to boiling. Add an excess of a concentrated solution of sodium thiosulphate. Basic thorium thiosulphate is precipitated in a flocculent mass which, after standing about 12 hours, is easily filtered and washed. The precipitate with its filter paper is digested in concentrated hydrochloric acid, and again treated with the thiosulphate so as to get rid of all but a trace of ceria which contaminated the first precipitate. The precipitate is dissolved in hydrochloric acid, and treated with oxalic acid as described above. The first filtrate contains the yttrium and cerium earths. The hydroxides are precipitated by ammonia, and separated by the double potassium sulphate process described on page 508 for separating zirconium and yttrium. The cerium salt, $Ce_2(SO_4)_3.3K_2SO_4$, is but sparingly soluble, while the yttrium salt, $Y_2(SO_4)_3.3K_2SO_4$, is readily soluble.

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[1] According to O. Hauser (*Zeit. anal. Chem.*, **47**. 677, 1908), the presence of uranyl salts makes the cerium oxalates very soluble, unless a great excess of oxalic acid is added.

[2] The precipitated oxalates will be contaminated with phosphates, if phosphorus compounds be present. A reprecipitation may then be necessary; or the precipitate may be washed into a dish and digested with fuming hydrochloric acid, then warmed with oxalic acid and the whole diluted with water. In this way most of the phosphoric acid passes into solution.

[3] E. Hintz and H. Weber, *Zeit. anal. Chem.*, **36**. 213, 1897; P. Drossbach, *Zeit. angew. Chem.*, **14** 655, 1901; E. Benz, *ib.*, **15**. 297, 1902; O. Hauser and F. Wirth, *ib.*, **22**. 484, 1909; C. Glazer, *Zeit. anal. Chem.*, **36**. 213, 1897; R. J. Meyer and R. Jacoby, *ib.*, **27**. 364, 1901; R. Finkener, *ib.*, **3**. 369, 1864; N. Engström, *Zeit. Kryst.*, **3**. 191, 1879; W. Blomstrand, *ib.*, **15**. 99, 1889; H. Bäckström, *ib.*, **16**. 83, 1890; C. Jones, *Amer. Chem. Journ.*, **20**. 345, 1898; H. Gorceix, *Compt. Rend.*, **100**. 357, 1885; M. Holzmann, *Journ. prakt. Chem.* (1), **75**. 321, 1858; R. Ruer, *Zeit. anorg. Chem.*, **42**. 87, 1904.

[4] L. F. Nilson, *Ber.*, **13**. 1437, 1880; P. T. Cleve and M. Höglund, *ib.*, **6**. 1468, 1873; N. J. Berlin, *Pogg. Ann.*, **43**. 111, 1838.

No exact quantitative methods are known for separating the individual members of these groups, and all known methods give more or less approximate analytical separations. This is because the reactions of the different members of the group of rare earths, with the possible exception of cerium, differ among themselves by minute differences; so much so, that it is difficult to draw a real line of demarcation between the yttrium and cerium earths. In all attempts at separation it is necessary to dissolve and reprecipitate a number of times, and in some cases an elaborate process of fractional crystallisation must be employed. These methods fall outside the range of analytical work, and details must be sought in the original memoirs.

Opening the Minerals.—The minerals containing the rare earths are opened by the usual methods.[1] When sulphuric and hydrofluoric acid are employed, the fluorine is driven off by heating. If hydrochloric acid be used, the solution is evaporated to dryness to make the silica insoluble. The residue is treated with a little hydrochloric acid, diluted with water, and filtered. If sulphuric acid, or potassium pyrosulphate or bisulphate, be employed for opening the mineral, the mass must be stirred with cold water to get the required solution; otherwise, titanium hydroxide may be precipitated. If hydrofluoric acid alone be employed in the cold, a gelatinous precipitate of the silico-fluorides and fluorides of the earths is obtained. The precipitate is collected and washed with dilute hydrofluoric acid. Niobium, tantalum, zirconium, etc., pass into solution.[2] The insoluble fluorides are decomposed by sulphuric acid. Fusion of the mineral with sodium or potassium hydroxides or carbonates, and leaching with water, gives a residue of insoluble hydroxides.

§ 266. The Determination of "Rare Earths" in Silicates.

The determination of zirconium in silicates has been discussed on page 498. If rare earths be also present, they will be found in the filtrate from the zirconium. Several methods of separating the rare earths are available. The following process is adapted for silicates containing but small quantities of the rare earths. It is based upon the very sparing solubility of the fluorides of the rare earths and thorium, and the ready solubility of the fluorides of the remaining elements (including zirconium, if present) in dilute hydrofluoric acid.[3]

Start with the filtrate from the zirconium phosphate (page 498), which we can suppose contains salts of the rare earths, beryllium, titanium, aluminium, iron, and uranium. Treat the solution with an excess of sodium hydroxide, in which beryllium, uranium, and aluminium hydroxides are soluble, while titanium, iron, and the rare earth hydroxides are almost insoluble. Dilute the solution. Decant the clear through a filter paper; wash the precipitate twice by decantation; and then wash the precipitate into a platinum dish.

Treat the precipitate with hydrofluoric acid; evaporate the mixture nearly to dryness; and add a little water with a few drops of hydrofluoric acid. Collect the insoluble precipitated fluorides on a filter paper, using a rubber funnel and platinum cone. Wash the precipitate with water acidulated with hydrofluoric acid, and finally transfer the precipitate to a platinum dish.

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[1] H. B. Hicks (*Journ. Amer. Chem. Soc.*, **33**. 1492, 1911) recommends sulphur monochloride vapour for opening the rare earth minerals. Volatile chlorides are formed. This treatment decomposes rutile, wolframite, scheelite, tantalite, chromite, etc. See also E. F. Smith, *ib.*, **22**. 289, 1898; R. D. Hall, *ib.*, **26**. 1243, 1904.

[2] M. Delafontaine, *Chem. News*, **75**. 229, 1897.

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **176**. 77, 1900; J. J. Chydenius, *Pogg. Ann.*, **119**. 49, 1861; M. Delafontaine, *Chem. News*, **75**. 229, 1897; J. J. Berzelius, *Pogg. Ann.*, **16**. 385, 1829; A. Rosenheim, V. Samter, and I. Davidsohn, *Zeit. anorg. Chem.*, **35**. 424, 1903.

Evaporate the solution to dryness with sulphuric acid, to decompose the fluorides. Ignite the filter paper separately, and add the ash to the contents of the dish. Dissolve the residual sulphates in dilute hydrochloric acid; precipitate the rare earths with ammonia; redissolve the precipitate in hydrochloric acid; and evaporate to dryness.

Treat the residue with a few drops of an aqueous solution of oxalic acid; filter, and wash the insoluble oxalates. Dry the precipitate; ignite the oxalates; weigh the resulting oxides; and report as "rare earths."

§ 267. The Analysis of a Mixture of Rare Earths.

The analysis of a "rare earth mineral," and the separation of some of the more important members of the rare earth group, is well illustrated by the following method for the analysis of monazite sands, etc.[1] The analysis occupies about seven days.

1. *The Fusion.*—About a gram [2] of the finely powdered mineral is fused in a platinum crucible with five to six times its weight of sodium pyro- or bisulphate.[3] The temperature is raised very gradually to a red heat so as to avoid loss by spurting. The fusion temperature is kept as low as possible to avoid the formation of sparingly soluble basic sulphates. When all is dissolved, the crucible and contents are allowed to cool. The cold cake is taken up with cold water, and evaporated to dryness on a sand bath. Digest the residue in 10 c.c. of concentrated sulphuric acid, pour the solution into 200 c.c. of cold water, and boil the mixture in a flask with a reflux condenser for two or three hours. Most of the zirconia and ferric oxide dissolve. Silica, titanic, niobic, and tantalic oxides,[4] etc,[5] are precipitated. Filter. Let the solution stand 24 hours, and re-filter if necessary. Wash the precipitate, which may contain the tungstic, stannic, titanic, tantalic, and niobic oxides and part of the zirconia and ferric oxide. The filtrate contains the rare earth oxides, uranium and thorium oxides, alumina, part of the zirconia and ferric oxides, the alkaline earths, etc.

2. *The Separation of Tin, Tungstic, Titanic, Tantalic, and Niobic Acids.*—Digest the residue with ammonium sulphide so as to remove the stannic and tungstic oxides (page 406). The insoluble mass is treated with a mixture of equal volumes of 10 per cent. sulphuric acid and 3 per cent. hydrogen peroxide.[6] Dilute the filtrate to 200 c.c., add sulphurous acid, and boil in a large flask fitted with a reflux condenser (fig. 128) until a little of the clear gives no titanium coloration when tested with hydrogen peroxide. About two or three hours' boiling suffices to precipitate all the titanium, tantalum, and niobium oxides. The ferric oxide and zirconia remain in solution.[7] Filter off the insoluble residue, and wash. Add the filtrate and washings to the main solution, or determine the iron and zirconium they contain as indicated below.

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[1] C. Glaser, *Journ. Amer. Chem. Soc.*, 18. 782, 1896; *Chem. Ztg.*, 20. 619, 1896; *Zeit. anal. Chem.*, 36. 213, 1897; *Chem. News*, 75. 145, 157, 1897; G. Chesneau, *Compt. Rend.*, 153. 429, 1911.

[2] More frequently between 10 and 30 grms. are taken if some of the rarer of the "rare earths" are to be determined by the process here described.

[3] The sodium salt is preferred to the potassium salt because the latter forms sparingly soluble double sulphates with some of the oxides under investigation.

[4] A trace of tantalic oxide and silica may dissolve in the sodium bisulphate solution.

[5] Lead and barium sulphates, if present, remain undissolved; so also do the stannic and tungstic oxides.

[6] L. Weiss and M. Landecker, *Zeit. anorg. Chem.*, 64. 65, 1909.

[7] Or, if necessary, fuse with potassium bisulphate. Cold water must be used in dissolving the cake of the bisulphate fusion.

3. *Separation of Titanic Oxide from Niobic and Tantalic Oxides.*—The moist residue is boiled three or four hours with a large excess of salicylic acid. The titanic oxide dissolves, while the niobic and tantalic oxides remain insoluble.[1] The filtrate and washings are treated with ammonia, and the titanic hydroxide is filtered off, washed, ignited, and weighed as TiO_2. The niobic and tantalic oxides are calcined and weighed. If desired, the two last-named oxides can be separated by Marignac's process (page 421).

4. *Separation of the Hydrogen Sulphide Group.*—Saturate the hot acidified solution with hydrogen sulphide, and, when cold, again saturate the solution with the same gas. The members of the hydrogen sulphide group are precipitated. Filter, and boil the filtrate to expel the hydrogen sulphide. The residue on the filter paper contains the metals of the hydrogen sulphide group—copper, bismuth, etc. These, if present, are separated as described on page 319.

5. *Separation of the Thorium and Cerium Group from the Zirconium and Yttrium Groups.*—Thorium oxalate is somewhat soluble in nearly neutral solutions of ammonium oxalate,[2] and if a large excess of ammonium oxalate be used, thorium may not be precipitated at all. But an excess is necessary to keep the zirconium oxalate in solution. Hence, some thorium may escape precipitation, and, if not separated, will, later on, appear with the zirconium precipitate. Glaser therefore recommended adding concentrated hydrochloric acid to the boiling filtrate. On cooling, insoluble thorium oxalate is precipitated. The zirconium oxalate is soluble in the oxalic acid liberated by the action of the hydrochloric acid.[3]

The method here employed is based on the solubility of yttrium and zirconium oxalates and the "insolubility" of thorium and cerium oxalates in nearly neutral solutions of ammonium oxalate in the presence of hydrochloric acid. An alternative process is indicated on page 501.[4] Either evaporate the filtrate and washings from the preceding operation to about 100 c.c.; or treat the solution with ammonia so as to precipitate the phosphates and hydroxides of the rare earths, thorium, zirconium, aluminium, iron, and manganese. Filter and wash (page 183). Dissolve the precipitate in nitric or hydrochloric acid. The filtrate contains the alkaline earths. Nearly neutralise the solution (sulphates, nitrates, or chlorides) with ammonia, so that the solution has the least possible excess of acid. Boil. Add a large excess of a boiling solution of ammonium oxalate. Dilute the solution to nearly twice its volume with water, and add concentrated hydrochloric acid, drop by drop, until the addition of more acid to the clear solution produces no further precipitation. Let the mixture stand overnight. Filter off the precipitated oxalates, and wash with a solution of ammonium oxalate.[5] The precipitate contains the cerium earths, and the thorium as oxalates.[6] The filtrate is reserved for the determination of phosphorus, aluminium, iron, manganese, yttrium, zirconium, calcium, etc. Ignite the mixed precipitates to convert the thorium, cerium, lanthanum, and didymium oxalates into oxides.[1]

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[1] M. Dittrich and S. Freund, *Zeit. anorg. Chem.*, **56**. 344, 346, 1908; O. Hauser and H. Herzfeld, *Zentr. Min.*, 759, 1910.

[2] J. F. Bahr, *Liebig's Ann.*, **132**. 231, 1864.

[3] But even with Glaser's improvement the operation is not altogether satisfactory. The thorium and zirconium may be first removed by Metzger's process, and the thorium and zirconium separated by the oxalic process. The method indicated above will usually satisfy commercial requirements.

[4] The presence of uranium salts augments the solubility of cerium and lanthanum oxalates, and therefore the precipitation will be imperfect in the presence of uranium salts, unless a large excess of oxalic acid is added—O. Hauser, *Zeit. anal. Chem.*, **47**. 665, 1908.

[5] Dissolve, say, 2 grms. of solid ammonium oxalate in a little water, and make the solution up to 100 c.c.

[6] E. Hintz and H. Weber, *Zeit. anal. Chem.*, **36**. 27, 1897; P. Drossbach, *Zeit. angew. Chem.*, **14**. 655, 1901; E. Benz, *ib.*, **15**. 297, 1902; T. Scheerer, *Pogg. Ann.*, **56**. 498, 1842; **51**. 470, 1840; C. Rammelsberg, *ib.*, **108**. 48, 1859; H. Rose, *ib.*, **118**. 502, 1863; T. Thomson, *Trans. Roy. Soc. Edin.*, 6. 371, 1811; A. Connell, *Edin. Phil. Journ.*, **20**. 300, 1842; R. Hermann, *Journ. prakt. Chem.* (1), **82**. 387, 1861; M. Holzmann, *ib.* (1), **84**. 78, 1861;

I. *The Ammonium Oxalate Precipitate.*

6. *Separation of Thorium from Cerium, Lanthanum, and Didymium.*—This separation is based on the solubility of thorium oxalate, and the "insolubility" of cerium, lanthanum, and didymium oxalates, in a solution of ammonium oxalate containing a little ammonium acetate. A large excess of ammonium acetate should not be used, because cerium oxalate is slightly soluble in that reagent. When an excess of ammonium oxalate is present, a few c.c. of a solution of ammonium acetate will suffice to keep the thorium oxalate in solution.

Dissolve the mixed oxides in sulphuric acid, and nearly neutralise the solution with ammonia. Add to the boiling solution an excess of a boiling solution of ammonium oxalate. In a short time, when the oxalates of the cerium earths have formed, and before the liquid has cooled, add a solution of ammonium acetate.[2] Cerium oxalate will be precipitated, while thorium oxalate remains in solution. Let the solution stand overnight. Filter and wash. Dissolve the precipitate in sulphuric acid, and repeat the treatment, since otherwise some thorium will be precipitated, and, later, contaminate the cerium.[3]

7. *Determination of Thorium.*—Add an excess of ammonia to the filtrate, and thorium hydroxide will be precipitated. It is the general rule, in separating the rare earths in the presence of alkaline solutions, to dissolve the hydroxide, and reprecipitate; since the hydroxides are particularly liable to absorb alkaline salts from the mother liquid. The thorium hydroxide may be purified by dissolving the precipitate, well washed in boiling water, in nitric acid. Neutralise the solution with ammonia; add 10 per cent of ammonium nitrate[4] per 100 c.c. of solution; heat the solution between 60° and 80°; add 10 c.c. (per 50 c.c. of solution) of a 10 per cent. solution of hydrogen peroxide;[5] and boil the solution for a few minutes. A flocculent precipitate of thorium perhydroxide—$Th(OOH)(OH)_2$—separates. This can be easily washed.[6] Test some of the filtered solution by another treatment with an equal volume of hydrogen peroxide and boil. If no precipitate appears, filter the main solution while hot as rapidly as possible; and wash with a hot solution of 5 to 10 per cent. of ammonium

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T. Lange, *ib.* (1), **82**. 135, 1861; M. Delafontaine, *Liebig's Ann.*, **131**. 105, 1864; J. Brush and S. L. Penfield, *Amer. J. Science* (3), **25**. 459, 1883; G. Bodmann, *Zeit. anal. Chem.*, **27**. 251, 1901; H. du Bois and O. Liebknecht, *Ber.*, **32**. 3346, 1899.

[1] If much yttrium earths be present, the precipitate may be contaminated with them. The precipitate is then redissolved and the operations repeated. A similar remark applies if phosphorus be present.

[2] If the ammonium acetate be added before the oxalate precipitate has formed, the mixture is inclined to give a turbid filtrate.

[3] E. Hintz and H. Weber, *Zeit. anal. Chem.*, **36**. 27, 1897; E. Benz, *Zeit. angew. Chem.*, **14**. 297, 1902. For the solubility of thorium oxalate, see R. Bunsen, *Pogg. Ann.*, **155**. 380, 1875. E. Benz says that "under no circumstances is it possible to get a satisfactory separation of thorium from cerium by ammonium oxalate in the presence of ammonium acetate." If there is any difficulty, use Metzger's process, page 510.

[4] If the ammonium nitrate be omitted, it is so difficult to calcine the voluminous gelatinous precipitate without loss of fine dust, that it is advisable to dissolve the precipitate in hydrochloric acid, and reprecipitate with ammonia.

[5] Traces of phosphoric oxide, or traces of cerium, if present, will be precipitated as cerium phosphate, etc., with the thorium. If an appreciable time elapses between the precipitation and the filtration of the thorium hydroxide, the greater the risk of contamination with ceria.

[6] This behaviour with hydrogen peroxide distinguishes thorium and zirconium from cerium and yttrium compounds.

nitrate. Add the filtrates to the solution of cerium earths employed in the next operation. Wash the precipitate, ignite in a platinum crucible, and weigh as thorium oxide—ThO_2. The precipitate should be white.[1] If the precipitate has a yellow tinge, a little ceria may be present. A reprecipitation is necessary to get white thoria free from ceria.[2]

8. *Separation of Cerium from Lanthanum and Didymium.*—The precipitated cerium earths may be ignited and weighed as "cerium earths." The precipitate would include lanthana and didymia. To separate the cerium,[3] dissolve the mixed oxides in hot hydrochloric acid. Add a solution of potassium or sodium hydroxides, so as to precipitate the gelatinous hydroxides of cerium, lanthanum, and didymium. Wash the hydroxides three or four times by decantation; add a concentrated solution of potassium hydroxide so as to make the mixture occupy about 200 c.c. Pass a slow current of chlorine gas through the solution, and agitate the mixture from time to time. When the liquid no longer has an alkaline reaction, and is saturated with chlorine, the cerium hydroxide will have been oxidised to lemon-yellow cerium dioxide, which remains as an insoluble precipitate, whereas the lanthanum and didymium hydroxides will have dissolved.[4] Let the mixture stand in a corked flask for 24 hours. Filter, and wash the cerium dioxide. While the precipitate is still moist, dissolve it in hydrochloric acid. Add ammonium oxalate to the solution. Wash and ignite the precipitated cerium oxalate, and weigh as cerium oxide—CeO_2. Cerium oxide has a light rose colour, and it dissolves forming a yellow solution in sulphuric acid. The colour is bleached by the addition of sulphurous acid, and restored by the addition of hydrogen peroxide or sodium peroxide.

9. *Determination of Lanthanum and Didymium.*—Owing to the laborious nature of the process for the separation of these two bases, they are often precipitated together as oxalates in the filtrate from the cerium dioxide, calcined, and weighed as a mixture of "$La_2O_3 + Di_2O_3$."[5] Damour and Deville's process[6] of separation is based on the fact that, when a mixture of didymium and lanthanum nitrates is heated, the didymium nitrate decomposes before the lanthanum nitrate and forms a sparingly soluble didymium subnitrate.

The filtrate from the cerium dioxide is boiled to eliminate the chlorine, and treated with an excess of ammonia. The precipitated didymium and lanthanum hydroxides are washed, and dissolved in nitric acid. The solution is evaporated to dryness in a small weighed platinum basin. The dried mass usually has a pale rose colour. Heat the basin to a temperature of about 450° in a small muffle.[1] Care must be taken not to overheat the mixed salts near the bottom of the basin. The salts fuse and give off nitrous fumes. It is difficult to ensure uniform heating if a large quantity of the mixed nitrates is being treated. The result is better when small quantities are treated. In about half a minute remove the basin from the source of heat. When nearly cold, add hot water. The lanthanum nitrate dissolves, while greenish-grey flakes of didymium subnitrate remain undissolved. After the mixture has stood a couple of hours, boil and filter. If the filtrate has a pink colour, evaporate again with nitric acid, and repeat the operation until a colourless liquid is obtained. Two or three repetitions of the process may suffice. According to Cleve, a repetition of the process fourteen times will give a solution in which the spectroscope can detect no didymium. The didymium subnitrate is calcined until its weight is constant, and weighed as didymium oxide—Di_2O_3. The didymia so obtained varies in tint from pure white to pale cinnamon brown—usually a pale yellowish-brown oxide is obtained which is readily soluble in dilute nitric acid.

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[1] P. T. Cleve, *Bull. Soc. Chim.* (2), **43**. 53, 1885; G. Wyrouboff and A. Verneuil, *ib.* (3), **19**. 219, 1898; *Chem. News*, **77**. 245, 1898; *Compt. Rend.*, **126**. 340, 1898; **127**. 412, 1898; **128**. 1331, 1899; L. de Boisbaudran, *ib.*, **100**. 605, 1864; E. Benz, *Zeit. angew. Chem.*, **15**. 297, 1902. For another method of purifying the thorium oxide, see page 510—Metzger's process.

[2] White thorium hydroxide, $Th(OH)_4$, readily dissolves in ordinary mineral acids; the oxide ThO_2 is practically insoluble in these acids, but it dissolves in hot fuming sulphuric acid, and it can be converted into a soluble sulphate by fusion with sodium pyrosulphate.

[3] G. Mosander, *Journ. prakt. Chem.* (1), **30**. 267, 1843; H. St C. Deville, *Compt. Rend.*, **59**. 272, 1864; P. Schützenberger, *Compt. Rend.*, **120**. 663, 962, 1143, 1895; **124**. 481, 1897.

[4] O. Popp (*Liebig's Ann.*, **131**. 359, 1864) used sodium hypochlorite in place of chlorine gas for the separation; W. Gibbs (*Zeit. anal. Chem.*, **3**. 396, 1864) oxidised the solution with lead peroxide; H. Zschiesche (*ib.*, **9**. 541, 1870), red lead; C. Winkler (*ib.*, **4**. 417, 1865; E. J. Roberts, *Amer. J. Science* (4), **31**. 350, 1911), potassium permanganate; O. N. Witt (*Chem. Ind.*, **11**. 19, 1896), sodium peroxide; G. Wyrouboff and A. Verneuil (*Bull. Soc. Chim.* (3), **19**. 219, 1898; *Chem. News*, **77**. 245, 1898), hydrogen peroxide; G. Bricout (*Compt. Rend.*, **118**. 145, 1894) suggested a separation based on the solubility of cerium carbonate in chromic acid; M. M. Pattison and J. Clarke (*Chem. News*, **16**. 259, 1867) decomposed the chromate by heat, etc.; and H. Robinson (*ib.*, **54**. 229, 1886) based a process on the different solubilities of the nitrates.

[5] The term "didymium" is here used for a mixture of praseodidymium and neodidymium.

[6] E. Damour and H. St C. Deville, *Bull. Soc. Chim.* (2), **2**. 339, 1864; P. Schützenberger and O. Boudouard, *Compt. Rend.*, **122**. 697, 1896; **123**. 782, 1896; **126**. 1648, 1898; L. F. Nilson, *ib.*, 88. 642, 647, 1879.

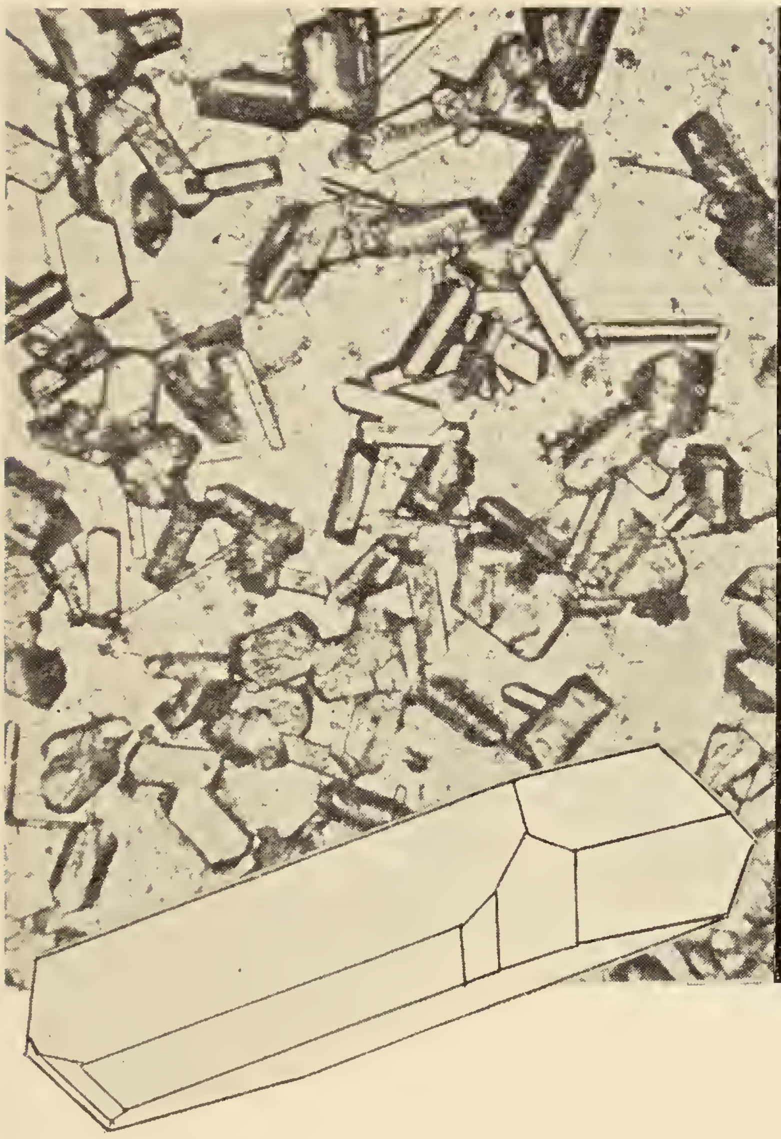

Fig. 158.—Didymium sulphate.

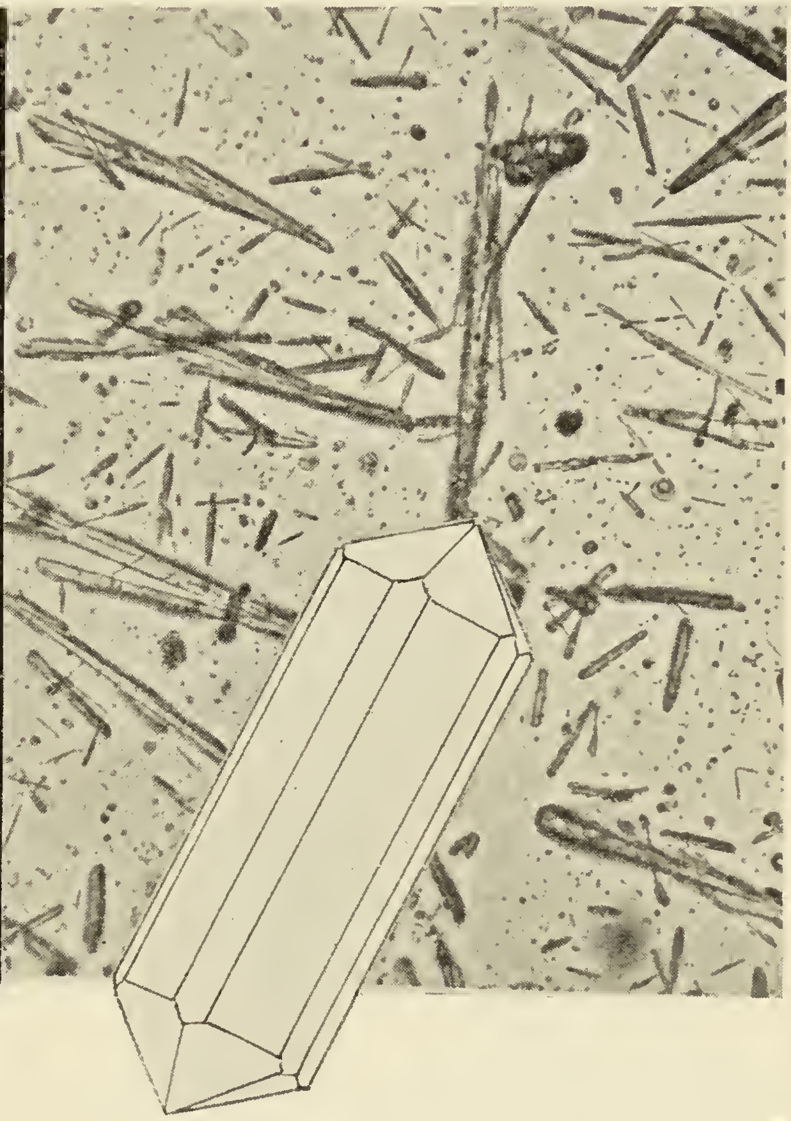

Fig. 159.—Lanthanum sulphate.

The lanthanum solution is also evaporated to dryness in a weighed dish, ignited, and weighed as lanthanum oxide—La_2O_3. A slight trace of lanthanum nitrate may be decomposed when the nitrates are calcined ; as a result, the amount of didymia—Di_2O_3—reported above is usually a little high, and the lanthania—La_2O_3—a little low. The lanthanum oxide generally has a pale yellowish-brown colour (if pure it would be white), and it is soluble in acids—*e.g.* dilute nitric acid.

When didymium oxide is treated with sulphuric acid, reddish-violet crystals

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[1] A small electric furnace with a pyrometer is excellent for the purpose.

(oblique rhomboidal prisms) of didymium sulphate (fig. 158) are obtained; while lanthanum sulphate furnishes colourless needles (right rhomboidal prisms) (fig. 159). Ideally perfect crystals are also shown in outline. Some needles of lanthanum sulphate can usually be detected among the plates of didymium sulphate, and conversely.

II. *The Filtrate from the Ammonium Oxalate Precipitate.*

10. *Determination of Aluminium and Phosphorus.*—Add an excess of ammonia to the solution[1] remaining after the separation of the oxalates of the thorium and cerium groups. Filter and wash the precipitated hydroxides and phosphates. The filtrate may contain traces of cerium and thorium, which are usually neglected. The washed precipitate is dried and fused with sodium carbonate. The cold cake is extracted with water. Filter and wash the insoluble matter. The solution contains sodium phosphate and sodium aluminate. Bring the solution to a definite volume, and determine the phosphorus in one portion (page 595), and the combined aluminium and phosphoric oxides in another (page 182).

11. *Determination of Calcium.*—Dissolve the insoluble residue left, after leaching the sodium carbonate fusion with water, in dilute hydrochloric acid.[2] Add ammonia, filter and wash. Precipitate the lime as calcium oxalate from the filtrate in the usual manner (page 213).

12. *Determination of Iron and Manganese.*—Dissolve the precipitate in hot dilute hydrochloric acid, and neutralise the solution with dilute ammonia. Pour the solution slowly, with constant stirring, into a cold mixture of ammonium carbonate and sulphide.[3] Iron and manganese sulphides are precipitated, while zirconium, beryllium, and yttrium remain in solution. The precipitated iron and manganese sulphides can be separated in the usual manner.

13. *Separation of Beryllium from Zirconium and Yttrium.*—Boil the filtrate for an hour; beryllium, zirconium, and yttrium hydroxides are precipitated. Filter and wash. Dissolve the precipitate in dilute hydrochloric acid.[4] Treat the solution with an excess of sodium hydroxide, when zirconium and yttrium hydroxides are precipitated. The beryllium remains in solution. Boil the diluted filtrate one hour, when beryllium hydroxide is precipitated. Wash the precipitate, and treat as described on page 449.

14. *Separation of Zirconium and Yttrium.*—This separation[5] is based on the fact that potassium yttrium sulphate, $Y_2(SO_4)_3.3K_2SO_4$, is soluble in 7 to 8 parts of a feebly acid solution of potassium sulphate, while the corresponding potassium zirconium sulphate is practically insoluble in the same menstruum.[6]

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[1] This solution may contain aluminium, phosphorus, iron, manganese, calcium, magnesium, beryllium, zirconium, and yttrium.

[2] To make sure that all the zirconium is dissolved, incinerate the filter paper, and fuse with a little sodium carbonate. Add the solution to the main solution.

[3] The amount of ammonium carbonate should more than suffice to retain the oxides of yttrium, beryllium, and zirconium in solution; and the ammonium sulphide should suffice to precipitate all the iron and manganese.

[4] Or add hydrochloric acid to the solution and boil to expel the carbon dioxide. Cool, and treat the solution with sodium hydroxide, etc. Incinerate the filter paper as described in a preceding footnote.

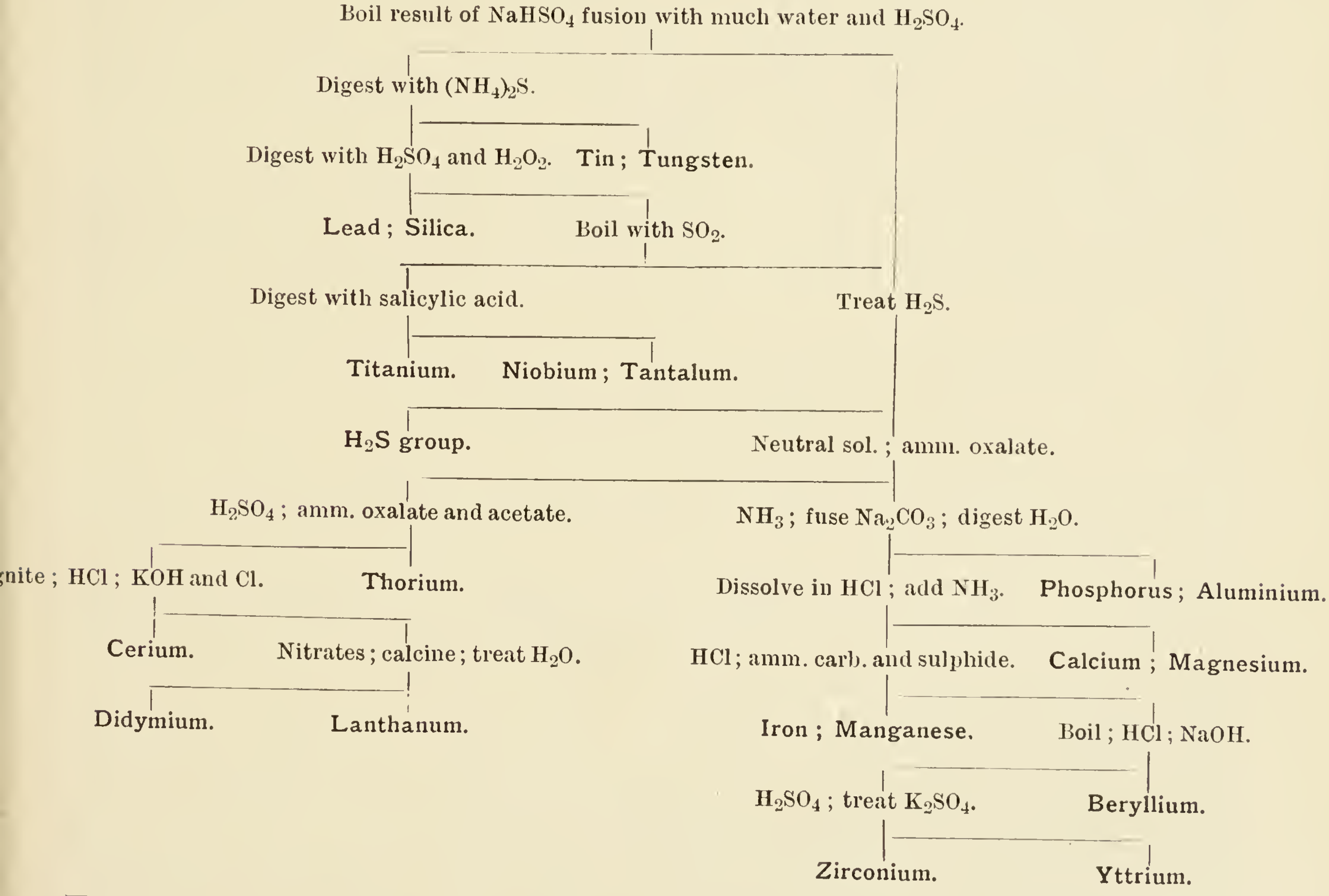
[5] J. J. Berzelius, *Pogg. Ann.*, **4**. 135, 1825; C. M. Warren, *ib.*, **102**. 449, 1857; E. Linnemann, *Monats. Chem.*, **6**. 335, 1885; C. Marignac, *Ann. Chim. Phys.* (5), **20**. 535, 1880; *Compt. Rend.*, **90**. 899, 1880; *Chem. News*, **41**. 250, 1880; M. Delafontaine, *ib.*, **11**. 241, 253, 1865; G. Krüss, *ib.*, **64**. 65, 75, 100, 120, 1891; *Liebig's Ann.*, **265**. 1, 1891; G. Urbain, *Ann. Chim. Phys.* (6), **19**. 184, 1900.

[6] When zirconia compounds are melted with potassium bisulphate, the insoluble double sulphate remains behind when the melted mass is extracted with water. Neither sodium nor ammonium sulphate can be used in place of the potassium salt, because they do not give a sparingly soluble double salt.

The operation is conducted in the following manner:—Dissolve the precipitate[1] containing the mixed zirconium and yttrium hydroxides in a little concentrated sulphuric acid.[2] Stir the ice-cold solution with a saturated solution of potassium sulphate.[3] This precipitates a double potassium zirconium sulphate[4]—possibly $Zr(SO_4)_2 . 2K_2SO_4 . 2H_2O$—which is practically insoluble in ice-cold water and in solutions of potassium sulphate. Hence, filter[5] and wash with a cold solution of potassium sulphate. The double sulphate is decomposed by boiling with a concentrated solution of sodium hydroxide. The compact zirconium hydroxide is washed, first by decantation, and then on the filter paper. The precipitate is dissolved in hydrochloric acid,[6] and reprecipitated with ammonia, filtered, washed, ignited, and weighed as zirconia—ZrO_2 (page 498).

The filtrate from the potassium zirconium sulphate is treated with an excess of ammonia.[7] The precipitate is filtered, washed, dissolved in acid, reprecipitated with ammonia, washed, ignited, and weighed as yttria—Y_2O_3. The yttrium so obtained is usually pale straw-yellow (if pure, it would be white), and soluble in warm acids.

The scheme of analysis may now be summarised (precipitates and solids on left, filtrates and solutions on right):—


Boil result of $NaHSO_4$ fusion with much water and H_2SO_4.
Digest with $(NH_4)_2S$.
Digest with H_2SO_4 and H_2O_2.
Tin ; Tungsten.
Lead ; Silica.
Boil with SO_2.
Digest with salicylic acid.
Treat H_2S.
Titanium.
Niobium ; Tantalum.
H_2S group.
Neutral sol. ; amm. oxalate.
H_2SO_4 ; amm. oxalate and acetate.
NH_3 ; fuse Na_2CO_3 ; digest H_2O.
nite ; HCl ; KOH and Cl.
Thorium.
Dissolve in HCl ; add NH_3.
Phosphorus ; Aluminium.
Cerium.
Nitrates ; calcine ; treat H_2O.
HCl ; amm. carb. and sulphide.
Calcium ; Magnesium.
Didymium.
Lanthanum.
Iron ; Manganese.
Boil ; HCl ; NaOH.
H_2SO_4 ; treat K_2SO_4.
Beryllium.
Zirconium.
Yttrium.

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[1] Incinerate the filter paper, etc., as indicated in a preceding footnote.

[2] Sulphuric acid is preferable to nitric and hydrochloric acids, since, if chlorides or nitrates be present, some yttrium may be precipitated.

[3] Potassium Sulphate.—The finely powdered salt is ground in a mortar with water at about 30°, but not at a higher temperature.

[4] The corresponding sodium and ammonium salts are fairly soluble in water.

[5] The precipitate sometimes sticks tenaciously to the sides of the beaker.

[6] The filter paper is incinerated, etc., as usual.

[7] C. Kersten, *Pogg. Ann.*, **47**. 392, 1839 ; H. Rose, *ib.*, **118**. 508, 1863 ; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **35**. 532, 1896 ; O. Boudouard, *Bull. Soc. Chim.* (3), **19**. 11, 1898 ;

§ 268. The Gravimetric Determination of Thorium—Metzger's Process.

Metzger's process[1] is based on the fact that a saturated solution of fumaric acid in 40 per cent. alcohol quantitatively precipitates white flocculent thorium oxide from neutral solutions containing 40 per cent. alcohol by volume. The only other metals precipitated are zirconium (completely), erbium (partially), silver, and mercury. The trial results are excellent. Cerium,[2] lanthanum, didymium, yttrium, samarium, gadolinium give no precipitates in hot or cold solutions under the same conditions. Similarly with salts of copper, gold, manganese, calcium, strontium, barium, zinc, cadmium, boron, aluminium, tin, lead, phosphorus, arsenic, antimony, bismuth, uranium, vanadium, tungsten, iron, cobalt, nickel, platinum.

First Precipitation.—The precipitated oxalates (page 504) are washed and rinsed into a beaker, mixed with 20–25 c.c. of concentrated caustic potash, and boiled. Dilute the solution with water, filter and wash. Dissolve the precipitated hydroxides in dilute nitric acid (1 : 1), and evaporate the solution to dryness on a water bath. Dissolve the residue in 50 c.c. of water, and add sufficient alcohol and water to make a solution containing 40 per cent. of alcohol, by volume, and occupying 200 c.c. Add 20 to 25 c.c. of fumaric acid,[3] and heat the solution to boiling. Filter while hot, and wash the precipitated thorium several times with hot 40 per cent. alcohol.

Second Precipitation.—Return the filter paper and the precipitate to a beaker. Add 25–30 c.c. of dilute hydrochloric acid (1 : 1). Heat the solution to boiling, and filter off the paper. Wash with dilute acid, and evaporate the filtrate and washings to dryness on a water bath. Agitate the solution, and wash down the sides of the basin every now and again, to prevent the residue clinging to the sides. While still on the water bath, loosen the residue from the bottom of the basin by stirring with a "policeman." The carbonaceous matter does not interfere. Add sufficient alcohol and water to make the solution occupy about 150 c.c.; add 10 c.c. of fumaric acid; and heat the solution to boiling. Filter, and wash with 40 per cent. alcohol. Ignite, and weigh as thorium oxide—ThO_2.

Evaluation of Thorium Minerals.[4]—The thorium minerals are evaluated on

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G. Krüss and L. F. Nilson, *Ber.*, **20.** 1677, 1887. According to C. F. Whittemore and C. James (*Journ. Amer. Chem. Soc*, **34.** 772, 1912) the precipitation of yttrium hydroxide by sodium or ammonium hydroxide gives high results in the presence of potassium or sodium salts, and they recommend one precipitation with ammonium sebacate in the presence of sodium salts, and two precipitations in presence of potassium salts.

[1] F. J. Metzger, *Journ. Amer. Chem. Soc.*, **24.** 901, 1902. A. C. Neish (*Journ. Amer. Chem. Soc.*, **26.** 780, 1904; *Chem. News*, **90.** 196, 201, 1904) separated thorium by metanitrobenzoic acid; L. M. Dennis and F. L. Kortright (*Amer. Chem Journ.*, **16.** 79, 1894; *Journ. Amer. Chem. Soc.*, **18.** 947, 1896), by potassium trinitride—KN_3: J. J. Chydenius (*Pogg. Ann.*, **119.** 45, 1861; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **35.** 530, 1896; J. P. Drossbach, *Zeit. angew. Chem.*, **14.** 656, 1901; E. Benz, *ib.*, **15.** 302, 1902), by boiling with sodium thiosulphate; T. O. Smith and C. James (*Journ. Amer. Chem. Soc.*, **34.** 281, 1912) by sebacic acid; and M. Koss (*Chem. Ztg.*, **36.** 686, 1912; A. Rosenheim, *ib.*, **36.** 821, 1912; F. Wirth, *Zeit. angew. Chem.*, **25.** 1678, 1912) by sodium hypophosphate. See also B. L. Hartwell, *Journ. Amer. Chem. Soc.*, **25.** 1128, 1903; *Chem. News*, **89.** 15, 27, 1904. Thorium is precipitated quantitatively by ammonium molybdate—F. J. Metzger and F. W. Zons, *Journ. Ind. Eng. Chem.*, **4.** 493, 1912.

[2] If much cerium be present, a little may be precipitated during the first precipitation of the thorium oxide.

[3] Fumaric Acid Solution.—Dissolve 1 grm. of fumaric acid in 100 c.c. of water. Fumaric acid costs about 2s. for 10 grms.

[4] E. White, *Thorium and its Compounds*, London, 1912; O. R. Böhm, *Die Fabrikation der Glühkörper für Gasglühlicht*, Halle a. S., 1910.

their thorium contents. Most of the commercial thoria comes from monazite sand, which has about 6 per cent. of ThO_2; a little comes from thorianite, which has about 80 per cent. of ThO_2. The following process of evaluation has been tacitly recognised by buyer and seller as a kind of standard:—

Heat 12·5 grms. of the sand to 180°–200° with 50 c.c. of concentrated sulphuric acid. In 2 or 3 hours the grains will be all broken up. Dilute the cold mixture with 300–400 c.c. of water, and filter. Make the solution up to 500 c.c. Agitate 200 c.c. (5 grms. of sample) with 180 c.c. of a cold saturated solution of oxalic acid. Let stand overnight (about 12 hours), and filter. Wash the precipitate with dilute hydrochloric acid or water until the runnings are free from phosphates. Reject the filtrates. Ignite the dried precipitate and dissolve it in hydrochloric acid (sp. gr. 1·16). Evaporate to dryness, add a few c.c. of water, and again evaporate to dryness. Dissolve the acid-free chlorides in 200 c.c. of water, and add 9 grms. sodium thiosulphate in 30 c.c. of water. After standing 12 hours, boil for 10 minutes, filter, and wash the precipitate until ammonia gives no turbidity. Boil the filtrate for an hour, and collect the precipitate A as before. Reject the filtrate. The first precipitate is dissolved in 5 per cent. hydrochloric acid. The acid solution is evaporated to dryness, taken up with 150 c.c. of water, and treated with 3 grms. of sodium thiosulphate as before. The filtrate is treated with ammonia and boiled. The precipitate is washed and mixed with the precipitate A. The thiosulphate precipitate is dissolved in acid, evaporated, etc., and treated with thiosulphate as before. The precipitate is washed until it gives no turbidity with ammonia. The filtrate is precipitated with ammonia, while the thiosulphate precipitate is again subjected to the preceding treatment until the filtrate gives no precipitate with ammonia. Three thiosulphate precipitations generally suffice. The last thiosulphate precipitate is dissolved in 5 per cent. hydrochloric acid, and the solution made up to 150 c.c.; 10 c.c. of hydrochloric acid are added, and then 30 c.c. of oxalic acid. The liquid is kept between 30° and 40° for 2 to 3 hours, and, after standing overnight, filtered, washed, dried, ignited, and weighed as ThO_2. The ammonia precipitates and the precipitate A are mixed and re-worked for thoria. The yield is about 0·005 grm., or 0·1 per cent. on the 5 grms. sample.

§ 269. The Volumetric Determination of Cerium—Knorre's Process.

Cerium can be determined volumetrically in the presence of thorium, lanthanum, and didymium, by Knorre's process.[1] This is based on the fact that cerous salts are oxidised to yellow ceric salts by the action of ammonium persulphate in sulphuric acid solution, and the ceric salts are reduced to colourless cerous salts by the action of hydrogen peroxide:

$$2CeO_2 + H_2O_2 = Ce_2O_3 + O_2 + H_2O.$$

If, therefore, an excess of a solution of hydrogen peroxide of known strength be added to the yellow ceric salt, the excess of hydrogen peroxide can be determined by back titration with potassium permanganate. With freshly prepared solutions of the ceric salts, the reduction with hydrogen peroxide is instantaneous and the permanganate is also decolorised at once. With solutions which have been exposed to the air for some time, the reduction may take a quarter of an hour. Hence, if an old solution be titrated with permanganate within a quarter of an hour after adding the hydrogen peroxide, the results will be low. When the reduction is completed, the total permanganate consumed with both old and new solutions is the same. If an old solution be boiled for a few minutes with dilute sulphuric acid, and cooled before adding the hydrogen peroxide, the rate of the reduction is accelerated.

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[1] G. von Knorre, *Zeit. angew. Chem.*, 10. 685, 717, 1897; *Ber.*, 33. 1924, 1900; A. Job, *Compt. Rend.*, 128. 101, 180, 1899; E. Hintz and H. Weber, *Zeit. anal. Chem.*, 37. 94, 504, 1908; *Chem. News*, 79. 25, 41, 1909; G. P. Drossbach, *Ber.*, 29. 2452, 1896; A. Waegner and A. Müller, *ib.*, 36. 282, 1903; F. J. Metzger, *Journ. Amer. Chem. Soc.*, 31. 523, 1909; L. Schneider, *Dingler's Journ.*, 269. 224, 1888; W. Muthmann and L. Weiss, *Liebig's Ann.*, 331. 1, 1904; R. J. Meyer and A. Schweitzer, *Zeit. anorg. Chem.*, 54. 104, 1907.

Oxidation of Cerous to Ceric Salts.—Acidify the solution in an Erlenmeyer's flask with dilute sulphuric acid, and add 2 grms. of ammonium persulphate to the cold solution. Heat the solution to boiling for a couple of minutes. Cool to between 40° and 60° by dipping the vessel containing the solution in cold water. Add half a gram of ammonium persulphate,[1] heat the solution to boiling for about 5 minutes; cool, add another half gram of the persulphate, and boil 15 minutes, adding more dilute sulphuric acid towards the end of the boiling in order to decompose all the ammonium persulphate. Cool.[2]

The Titration.—Acidify the solution with sulphuric acid, and then add an excess of hydrogen peroxide. The hydrogen peroxide is added from a burette until the solution is decolorised, and then a small excess of the peroxide is run into the solution. When the reaction between the yellow ceric salt and the hydrogen peroxide is over, titrate the residual hydrogen peroxide with potassium permanganate until the solution acquires a rose colour which persists for at least half a minute.[3]

Calculation.—Suppose that 12·2 c.c. of the permanganate solution are required, and suppose that 25 c.c. of hydrogen peroxide were added to the solution, and that 25 c.c. of the peroxide require 29·8 c.c. of permanganate. The ceric salts in the solution correspond with 29·8 less 12·2 = 17·6 c.c. of the permanganate. The reaction between the permanganate and the hydrogen peroxide is represented by the equation:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

On comparing this equation with that indicated on page 198, and with

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2,$$

it follows that 55·84 grms. of Fe correspond with 140·25 grms. of Ce, or 172·25 grms. of CeO_2. It was found that 1 c.c. of the permanganate solution used in the above titration[4] corresponded with 0·00365 grm. Fe; hence, 1 c.c. will correspond with $0·00365 \times 3·0714 = 0·01121$ grm. CeO_2. Consequently 17·6 c.c. of the permanganate solution used in the back titration corresponded with $17·6 \times 0·01121 = 0·1973$ grm. CeO_2 in the given solution. Phosphoric and titanic acids disturb the action. The results are very fair if the above directions be carefully followed.

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[1] 3 grms. of ammonium persulphate suffice for the oxidation of 0·2 to 0·3 grm. cerium.

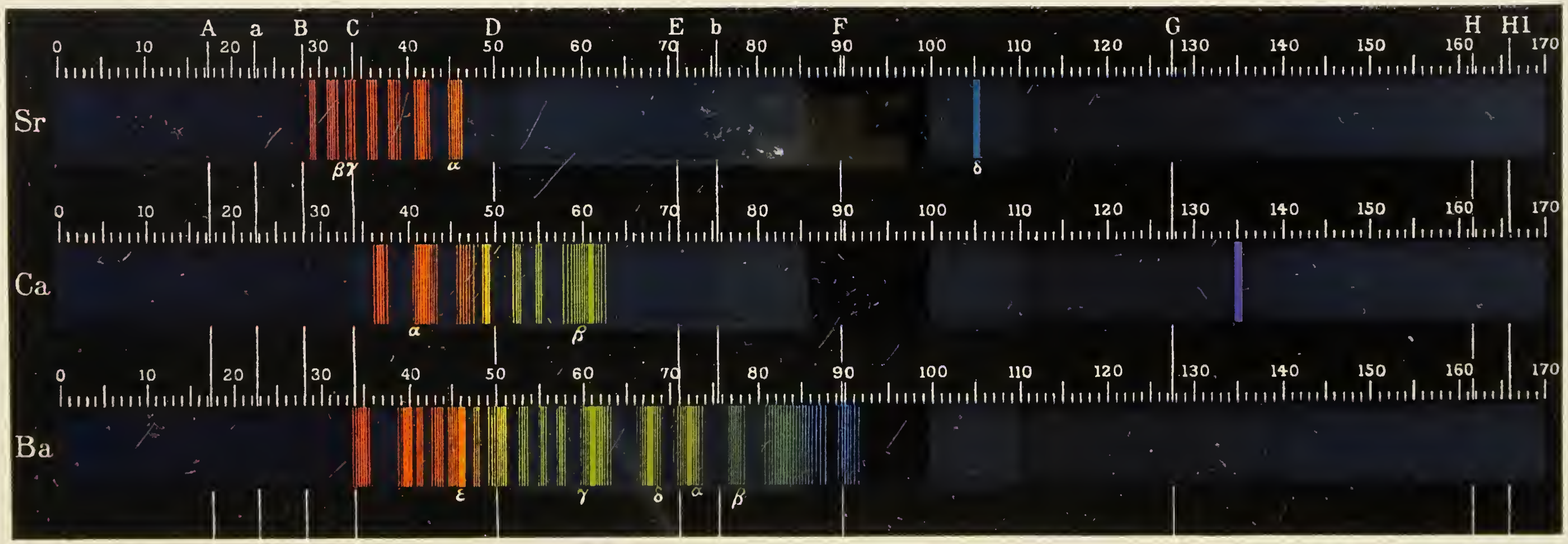
[2] Of course, if all the cerium is present as ceric sulphate, this preliminary oxidation is not needed.

[3] The slow decomposition of potassium permanganate by cerous sulphate does not interfere with the recognition of the end point in the permanganate titration.

[4] The permanganate solution should not be more concentrated than is represented by 2 grms. per litre.

PLATE I.

Chemical Analysis, J. W. Mellor, D.Sc.; London, Charles Griffin & Co., Ltd.



M^c Farlane & Erskine, Lith. Edin^r

SPECTRA OF METALS OF ALKALINE EARTHS (WITH FRAUNHOFER'S LINES OF SOLAR SPECTRUM AS STANDARDS OF REFERENCE.)

CHAPTER XXXVI.

SPECIAL METHODS FOR THE DETERMINATION OF BARIUM, STRONTIUM, CALCIUM, AND MAGNESIUM.

§ 270. The Influence of Barium and Strontium on the Calcium and Magnesium Precipitates.

THE spectroscopic test for barium and strontium is generally applied to the ignited calcium oxalate precipitate when these elements are sought in a silicate analysis.[1] These elements have characteristic spectra (Plate I.). It is assumed that sufficient barium and strontium will be precipitated with the lime to reveal their presence, in spite of the fact that barium and strontium oxalates are more

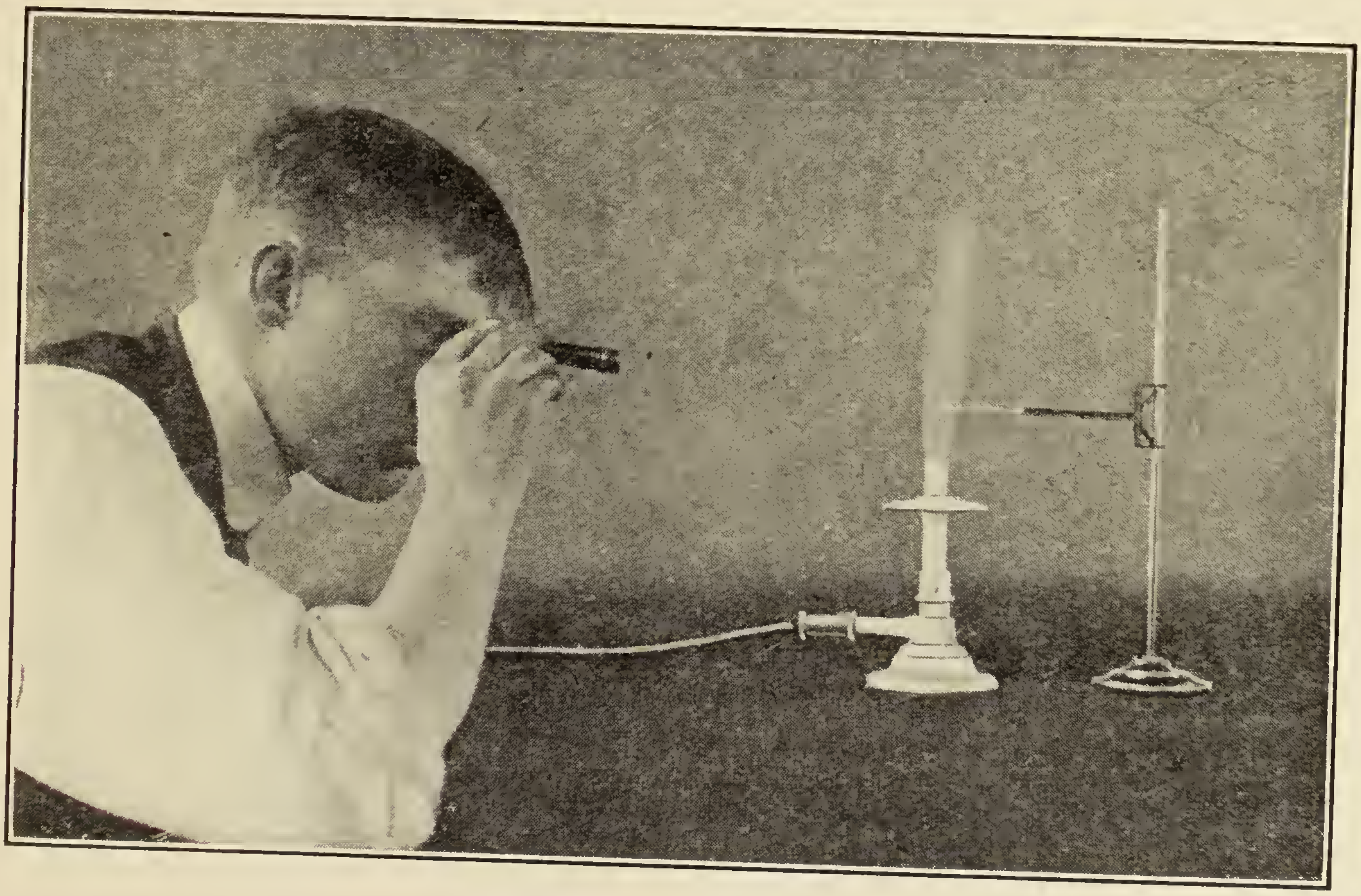


FIG. 160.—Spectroscopic Test.

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[1] A small direct-vision spectroscope with a scale is a very convenient adjunct for deciding if certain precipitates are properly washed. Fig. 160 illustrates the method of using the spectroscope. The loop of platinum wire in the Bunsen's flame (porcelain burner) has been dipped in a drop of the solution under investigation. F. von Kobell (*Journ. prakt. Chem.* (2), 3. 176, 1871) applies the spectroscope test to silicates by placing the powdered mineral, moistened with hydrochloric acid, on a piece of platinum foil, perforated with small holes and bent in the form of a trough. The arrangement is held in the flame by a pair of platinum-tipped tongs. The spectra of barium, strontium, and calcium are illustrated in Plate I. The spectroscopic method will detect $\frac{1}{1000}$ mgrm. of baryta; $\frac{6}{100,000}$ mgrm. of strontia; and $\frac{6}{100,000}$ mgrm. of lime (Bunsen).

soluble than the corresponding calcium oxalate. Hillebrand[1] says that "this assumption, in the case of strontium, is well founded, but it may be entirely fallacious in the case of barium." For instance, a mineral containing 0·76 per cent. of barium gave no indication of barium under the conditions of the test. This is due to the solvent action of ammonium chloride upon the barium oxalate. In a series of experiments with artificial mixtures of calcium with barium and with strontium, it was found that strontium and barium are but very incompletely precipitated by the addition of a slight excess of ammonium oxalate, but a greater proportion is precipitated when a large excess of ammonium oxalate is employed. With traces of strontium in the presence of a large excess of calcium, most of the strontium is precipitated with the calcium; but this action was not noticed with barium, since a considerable proportion of the barium escapes precipitation with the calcium, and is therefore to be sought in the filtrate. With a double precipitation of the lime, much of the strontium, and practically no barium, will be associated with the lime, provided the amount of barium does not exceed 0·2 or 0·3 per cent. If more than this amount of barium be present, the precipitation by ammonium oxalate can be repeated a third and fourth time, or the strontium and barium can be separated from the calcium; and the barium and strontium, which are recovered from the lime precipitate, can be separated by the process described below.

If barium be present, it may also contaminate the ammonium magnesium phosphate precipitate as barium phosphate. In that case, the barium must be removed[2] before precipitating the magnesium ammonium phosphate. Add 3 drops of sulphuric acid to the filtrate from the calcium oxalate; evaporate the solution to dryness; ignite the residue in a porcelain dish to drive off the ammonium salts; take the residue up with water acidulated with hydrochloric acid; filter off the carbonaceous matters; add a drop of sulphuric acid; let the mixture stand about 12 hours; and if a precipitate forms, filter, and treat the precipitated barium sulphate as described below. Determine the magnesia in the filtrate as indicated on page 218.

§ 271. The Separation of Calcium from Strontium and Barium—Stromeyer and Rose's Process.

If strontium be present, most of it will be found associated with the lime. The separation of barium and strontium is conveniently done by Stromeyer's process improved by Rose.[3] The mixed oxalates are ignited as usual and weighed as oxides.

Calcium.—The oxides are dissolved in dilute nitric acid (1 : 5) in a small 25-c.c. stoppered flask,[4] and the solution evaporated to dryness at 150° to 160° in a stream of dry air in an attachment resembling that employed for lithium

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[1] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **16**. 81, 83, 1894; *Bull. U.S. Geol. Sur.*, **422**. 120, 1910; *Chem. News*, **69**. 142, 147, 1894.

[2] R. Langley (*Amer. J. Science* (4), **26**. 123, 1908) removes the barium by precipitation with sulphuric acid just after the separation of silica; redissolves the precipitate in concentrated sulphuric acid, and reprecipitates it with water, in order to remove ferric and other sulphates.

[3] F. Stromeyer, *Gilbert's Ann.*, **54**. 245, 1816; H. Rose, *Pogg. Ann.*, **110**. 292, 1860; R. Fresenius, *Zeit. anal. Chem.*, **29**. 20, 143, 413, 1890; **30**. 18, 452, 583, 1891; **32**. 189, 1893; *Chem. News*, **68**. 213, 1893; J. L. M. van der Horn van der Bos, *Chem. Weekblad*, **8**. 5, 1911. P. E. Browning (*Amer. J. Science* (3), **43**. 50, 1892; (3), **44**. 462, 1892; *Chem. News*, **67**. 45, 53, 1893; **65**. 271, 282, 1892; **66**. 3, 1892) recommends amyl alcohol in place of the mixture of alcohol and ether employed in Stromeyer's and Rose's process; L. Moser and L. Machiedo (*Chem. Ztg.* **35**. 337, 1911) say that amyl alcohol offers no advantages over the ether-alcohol mixture.

[4] I use a weighing bottle like fig. 3, *b*, for this purpose.

(fig. 163, page 536). Treat the dry mass in the stoppered flask with about 10 times its weight of a mixture of equal volumes of ether and alcohol, in which the barium and strontium nitrates are but sparingly soluble,[1] while calcium nitrate is readily soluble. Let the flask stand about 12 hours, with occasional shaking. Filter through a small 5·5-cm. filter paper moistened with a couple of drops of the ether-alcohol mixture. Wash with the mixture of ether and alcohol until a drop of the filtrate gives no residue when evaporated to dryness on a clean piece of platinum foil[2]—about six washings usually suffice. Evaporate the filtrate to dryness. Dissolve the calcium nitrate in water, and precipitate the calcium as oxalate in the usual manner (page 213).

Strontium.—The strontium can be determined by difference, or directly. Dissolve the residue on the filter paper in dilute nitric acid; collect the washings in a 50-c.c. beaker and add sulphuric acid (1 : 2) almost equal in volume to the liquid in the beaker. In about 12 hours, filter off the precipitate, ignite,[3] and weigh as strontium sulphate—$SrSO_4$. The weight of strontium sulphate so obtained, multiplied by 0·5641, gives the corresponding amount of strontia—SrO.

Barium.—If barium be present in the calcium oxalate precipitate, it will also be found with the strontium sulphate. The barium and strontium can be separated by the chromate process described below.[4] If barium and strontium are to be determined, it is advisable to combine the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and then apply the chromate process to the combined filtrates. But there are so many leakages of barium, and other sources of error in the analysis, that it is best to determine the barium on a separate sample, either by the hydrofluoric decomposition process, or by the process of decomposition indicated on page 498.

§ 272. The Separation of Barium from Strontium and Calcium—Chromate Process.

The separation of barium, strontium, and calcium can be conveniently effected by (1) removing the calcium nitrate by Stromeyer and Rose's process, and then separating the barium and strontium by the chromate process; or (2) separating barium from the neutral solution of the mixed chlorides by the chromate process, precipitating the calcium and strontium as carbonates by means of ammonium or sodium carbonate, and after transforming the carbonates into nitrates, using Stromeyer and Rose's process for the calcium and strontium.

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[1] About 0·0017 per cent. of strontium nitrate.

[2] Take care that no flame is near the ether-alcohol. The mixture is very inflammable.

[3] If the ignition temperature be too high, some of the sulphate may decompose—M. Darmstadt, *Zeit. anal. Chem.*, **6**. 376, 1867. For the loss on heating strontium sulphate, see M. Darmstadt, *ib.*, **6**. 376, 1867; A. Mitscherlich, *Journ. prakt. Chem.* (1), **83**. 485, 1861; J. Boussingault, *Compt. Rend.*, **64**. 1159, 1867.

[4] A rough separation of barium from strontium can be effected by digesting the mixed sulphates in a cold concentrated solution of ammonium carbonate. Plug the narrow end of the funnel with a piece of cork, or use a funnel with a stopcock, and fill the funnel with the solution of ammonium carbonate Let the whole stand 12 hours. The strontium sulphate is converted into strontium carbonate, while the barium sulphate is but slightly affected. The precipitate is then washed with hot water, dilute hydrochloric acid, and finally with water. Ignite, and weigh as barium sulphate. The strontium is determined by neutralising the filtrate with ammonia, precipitation with ammonium carbonate, converting the ignited strontia into sulphate, and weighing as strontium sulphate. If the barium predominates, an appreciable quantity of strontium sulphate escapes decomposition; and when the strontium is in excess, an appreciable quantity of barium sulphate will be decomposed. R. Fresenius, *Zeit. anal. Chem.*, **29**. 20, 1890; S. G. Rawson, *Journ. Soc. Chem. Ind.*, **16**. 113, 1897; H. Rose, *Pogg. Ann.*, **95**. 286, 299, 427, 1855. See P. Schweitzer (*Contrib. Lab. State Univ.*, 1, 1876; *Proc. Amer. Assoc.*, 187, 1877) for the theory of the reaction. L. Moser and L. Machiedo (*Chem. Ztg.*, **35**. 337, 1911) consider the sulphate process gives an inexact separation of strontium, and believe that the best way of separating strontium from calcium and barium is to wash the anhydrous nitrates with a mixture of ether and alcohol. The strontium nitrate dissolves, while calcium and barium nitrates remain undissolved.

The transformation of the mixed carbonates or oxides into nitrates offers no particular difficulty; but in the case of the chlorides, repeated evaporation with concentrated nitric acid will not do, because the transformation is not complete.[1] It is then best to precipitate the carbonates with ammonium or sodium carbonate, and digest the carbonates with as little nitric acid as possible in a small flask, taking care, of course, to avoid loss by spurting.

First Precipitation of Barium Chromate.[2]—Evaporate the mixed nitrates to dryness, and dissolve the mixture in water. Neutralise any great excess of acid with ammonia, and add an excess, say 10 c.c., of a solution of ammonium acetate;[3] heat the solution to boiling, and gradually add, with constant agitation, 5 c.c. of ammonium bichromate solution.[4] Let the precipitate settle, and when the solution is cold, decant the clear liquid through a filter paper, and wash the precipitate by decantation with a dilute solution of ammonium acetate[5] until the filtrate is no longer perceptibly coloured. About 100 c.c. of liquid will be required for the washing. Some strontium, if present, may be carried down with the barium chromate; hence the precipitate is dissolved in dilute acid and reprecipitated.

Second Precipitation of Barium Chromate.—Place a beaker under the funnel and dissolve the precipitate on the filter paper by running warm dilute nitric acid (1 : 5) through the filter paper, and collect the "runnings" in the vessel in which the precipitation was first made. Wash the paper. Add ammonia to the solution until the precipitate which forms no longer redissolves when the solution is agitated. Add, with constant agitation, 10 c.c. of the concentrated solution of ammonium acetate; heat the solution to boiling. Let the solution settle till cold, and then filter through a weighed Gooch's crucible packed with asbestos felt. Wash the precipitate as before. Dry, ignite, and weigh as described on page 478.[6] The weight of the barium chromate multiplied by 0·60507 gives the corresponding amount of barium oxide—BaO.

Determination of Strontium.—The strontium may be precipitated from the combined filtrates by the addition of ammonia and ammonium carbonate after the solution has been concentrated in the presence of an excess of nitric acid. The precipitated strontium chromate may contain a little chromic acid. This is removed either by dissolving the precipitate in hydrochloric acid and precipitating the strontium as sulphate (page 515) in the presence of alcohol, if strontium alone and no calcium be present; or, by the application of the ether-alcohol process (page 514) in the event of both strontium and calcium being present.[7]

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[1] If magnesium be present, it too will be precipitated, and the chromium must later on be separated from the filtrate before the magnesium can be precipitated as phosphate. The chromium is separated by reducing the chromate as described on page 479, and precipitating the chromium as hydroxide by the addition of ammonia.

[2] The properties of barium chromate were discussed on page 477. It might be added that barium chromate is not soluble in water containing acetic acid when so much ammonium chromate is present that the solution contains only alkaline acetate and bichromate (H. N. Morse, *Amer. Chem. Journ.*, **2**. 176, 1880).

[3] AMMONIUM ACETATE.—Neutralise an aqueous solution of 300 grms. of "pure" commercial ammonium acetate with ammonia, and make the solution up to a litre. See R. Reik (*Monats. Chem.*, **23**. 1033, 1902), A. Mittasch (*Zeit. anal. Chem.*, **42**. 492, 1903), and L. H. Duschak (*Journ. Amer. Chem. Soc.*, **30**. 1827, 1908) for the impurities in the commercial salt.

[4] AMMONIUM DICHROMATE SOLUTION.—Dissolve 200 grms. of the salt in a litre of water.

[5] Made by diluting 20 c.c. of the above concentrated solution of ammonium acetate to a litre.

[6] Simply drying at 110° is not sufficient; the precipitate must be gently ignited (see page 478).

[7] For indirect method, claimed to be the most accurate, see R. L. y Gamboa, *Anal. Fis. Quim.*, **10**. 389, 1912.

Kämmerer[1] first used potassium chromate for the qualitative precipitation of barium in the presence of calcium and strontium from solutions containing acetic acid and ammonium acetate; Frerichs applied the reaction quantitatively; and Russmann showed that very fair results could be obtained with the process. Fresenius investigated the conditions which favoured success and failure; and Skrabal and Neustadl have developed the process in its present form, whereby a satisfactory separation can be made.

§ 273. The Determination of Barium in Insoluble Silicates.

Decomposition by Fusion with Sodium Carbonate.—It is not advisable generally to separate barium quantitatively from a solution which has previously been employed for the determination of the members of the hydrogen sulphide, ammonia, and ammonium sulphide groups, because of the leakage or loss of barium entailed during the separations. In the hydrogen sulphide group the main loss is due to the reduction of ferric chloride by hydrogen sulphide and oxidation of the sulphide to sulphate,[2] which means that barium sulphate will be precipitated. Curtman and Frankel found a loss of 14·7 mgrms. of barium in a solution containing 100 mgrms. of iron as ferric chloride per 100 c.c. when the ferric hydroxide was precipitated by ammonia, probably owing to the absorption of carbon dioxide by the ammonia. In the precipitation by ammonium sulphide, between 2 and 3 mgrms. of barium were also lost. Losses of barium may also occur owing to the presence of traces of sulphates in the reagents, and also to the retarding influence of ammonium salts on the precipitation of barium sulphate or carbonate. Hence it is best to determine barium on a special sample, and not on the sample used for the determination of silica, iron, etc.

On page 497, it may be remembered, the silicate was fused with sodium carbonate, the resulting "cake" was digested with water, and the residue treated with sulphuric acid for the determination of zirconium. The insoluble portion contained the barium, strontium, calcium, silica, etc.

To determine the total barium, ignite the filter paper containing the insoluble residue. Fuse with a gram of sodium carbonate for 10 to 15 minutes. Dissolve the mass in warm water, filter and wash. Place a 250-c.c. beaker below the funnel, and dissolve the precipitate in dilute hydrochloric acid. Wash the filter paper well. Neutralise the filtrate with sodium carbonate and make the solution up to 150 c.c., so that the solution occupies at least 30 c.c. per gram of calcium, barium, and strontium oxides present. This prevents the precipitation of calcium sulphate later on. Precipitate the barium by the addition of a hot solution of dilute sulphuric acid (1 : 300) to the boiling solution. The addition is made gradually, with constant stirring. The reasons will appear from the discussion on page 618. Wash by decantation;[3] collect the precipitate in a small filter paper; and ignite the barium sulphate, with the precautions indicated on page 616. The weight of the barium sulphate multiplied by 0·6570 gives the corresponding amount of barium oxide—BaO.

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[1] H. Kämmerer, *Zeit. anal. Chem.*, **12**. 375, 1873; J. Meschezerski, *ib.*, **21**. 399, 1882; E. Fleischer, *ib.*, **9**. 97, 1870; R. Fresenius, *ib.*, **29**. 20, 143, 413, 1890; **30**. 18, 452, 583, 1891; **32**. 183, 312, 1893; A. Skrabal and L. Neustadl, *ib.*, **44**. 742, 1906; W. Fresenius and F. Ruppert, *ib.*, **30**. 672, 1891; A. Russmann, *ib.*, **29**. 447, 1890; *Chem. News*, **63**. 13, 44, 1891; P. Schweitzer, *Proc. Amer. Assoc.*, 187, 1877; H. Baubigny, *Bull. Soc. Chim.* (3), **13**. 326, 1895; H. Baubigny, *ib.* (4), **1**. 55, 1907; H. Caron and M. Raquet, *ib.* (3), **35**. 1061, 1906; F. Frerichs, *Ber.*, **7**. 800, 956, 1874; H. Robin, *Ann. Chim. Anal.*, **18**. 445, 1903; B. Kahan, *Analyst*, **33**. 12, 1908; J. L. M. van der Horn van der Bos, *Chem. Weekblad*, **8**. 5, 1911; **9**. 1002, 1912; E. Beyne, *Chimiste*, **3**. 256, 1912—Sr in zinc blendes.

[2] L. J. Curtman and E. Frankel (*Journ. Amer. Chem. Soc.*, **33**. 724, 1911) found a loss of 1·4 mgrms. from this cause; A. A. Noyes and W. C. Bray (*ib.*, **29**. 137, 1907) state that the presence of 500 mgrms. of $FeCl_3$ in solution leads to the precipitation of as much as 20 mgrms. of barium as sulphate in the hydrogen sulphide group.

[3] The filtrate contains some silica, titanium, iron, aluminium, niobium, tantalum, and tin, if these elements be present.

Purification from Calcium.—If much calcium be present, the ignition should be made in a platinum crucible, and the ignited precipitate fused with sodium carbonate. The resulting "cake" is treated with water, and acidified with acetic acid, which is added drop by drop. The barium is precipitated by the addition of sulphuric acid as before.[1]

Hydrofluoric Acid Decomposition. — The total barium is conveniently determined in silicates[2] by treating 2 grms. of the finely powdered, dry (110°) silicate with 10 c.c. of sulphuric acid (1 : 4) and 5 c.c. of hydrofluoric acid in a large platinum crucible. Evaporate the solution on a water bath; add more hydrofluoric acid; and repeat the evaporation. If no sandy grains can be detected with the platinum spatula, further treatment with the hydrofluoric acid is not necessary. Heat the mixture until most of the sulphuric acid has been driven off. Let the crucible cool, and pour its contents into, say, 25 c.c. of water. The precipitate of barium sulphate will probably be free from calcium, but a little strontium may be present. Filter off the barium sulphate. Ignite in a platinum crucible; cool.

Purification from Calcium and Strontium.—The strontium and calcium can be removed by dissolving the barium sulphate in concentrated sulphuric acid, and again pouring the solution into water. If the amount of barium sulphate be less than about 0·002 grm., there is no need to purify the salt further.[3] Ignite the precipitated barium sulphate in a platinum crucible, and weigh as barium sulphate. This weight, multiplied by 0·6570, gives the corresponding amount of BaO.

§ 274. The Complete Analysis of Limestones, Gault Clays, etc.

Limestones, gault clays, marls, dolomite, magnesite, and similar carbonate rocks may be analysed from several different points of view; and, in consequence, a more or less incomplete analysis may serve all requirements. Some abbreviated methods will be described later.

Dissolution of the Sample.—A gram of the powdered and dried material is digested in a 100-c.c. beaker with 20 c.c. water, and 2 c.c. of concentrated hydrochloric acid and 2 drops of nitric acid. The acids are added slowly, and the beaker is kept covered by a watch-glass with its convex side downwards, so as to avoid loss during the effervescence. When effervescence has ceased, heat the solution to its boiling point on a hot plate, so as to drive off the carbon dioxide. Rinse the watch-glass with water. Filter the solution into an evaporating basin, and wash with water. Ignite the insoluble residue in a platinum crucible,[4] and fuse with a little sodium carbonate. Remove the fused mass with water and dilute hydrochloric acid: keep the crucible covered during the action to avoid loss by spurting. Add the solution to the main solution.

If the limestone does not contain much more than about 5 per cent. alumina and ferric oxide, and 15 per cent. of silica, strong ignition over a blast[1] in a covered platinum crucible will frequently give a powder wholly soluble in hydrochloric acid (1 : 1), except, possibly, a little flocculent silica which does not matter. If too much siliceous matter be present to render this treatment successful, as is sometimes the case with siliceous limestones, magnesian limestones, cement rocks, and highly calcareous marls, Meade[2] recommends igniting the limestone with just less than its own weight of sodium carbonate. The sintered, not fused, mass is then easily broken down by hydrochloric acid (1 : 1).

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[1] Silica is not precipitated with barium sulphate from dilute solutions of sodium silicate.

[2] With glazes, lead sulphate may be present. This can be removed by digestion with ammonium acetate as decribed on page 316.

[3] If zirconium be present, it will be associated with the barium sulphate, and it must be removed as indicated on page 498.

[4] The insoluble residue is sometimes reported as such, or as "siliceous minerals," "clay and sand," etc. As a matter of fact, the term "insoluble residue" is more or less ambiguous, since the attack on the siliceous minerals is dependent on the strength of the acid, and on the state of subdivision of the powder. The finer the sample is ground, the less the "insoluble residue."

Determination of Silica, Alumina, Titanium, etc.—Evaporate[3] the combined filtrates to dryness for silica (page 167); determine the alumina, titanium, iron, phosphorus,[4] lime,[5] magnesia, and manganese[6] as described for clays (pages 177 *seq.*). The carbon dioxide (page 553), water (page 571), and the alkalies are determined on separate samples.[7]

Chlorine and Fluorine.—For the chlorine, digest, say, 10 grms. with water and nitric acid at a gentle heat. Filter, and proceed by the method of page 652. For the fluorine, digest 10 grms. of the dry powdered sample in acetic acid[8] without boiling or filtering until the magnesium and calcium carbonates are decomposed. Evaporate the solution to dryness to expel the excess of acetic acid, add a slight excess of sodium carbonate, extract the residue with water; and the precipitate of calcium fluoride, carbonate, and insoluble residue is treated by the process of page 639.

Determination of Sulphur.—Sulphides as well as sulphates are often present in limestones and calcareous clays. To determine the "sulphate or soluble sulphur," digest, say, 2 grms. of the powdered sample in a large porcelain basin with 40 c.c. of water and 4 c.c of concentrated hydrochloric acid. Evaporate the solution to dryness. Boil the residue with water, filter and wash.[1] Precipitate the sulphuric acid in the filtrate as barium sulphate by the method of page 618. The weight of barium sulphate so obtained, multiplied by 0·3430, represents the corresponding amount of sulphur trioxide—SO_3; and when multiplied by 0·5833, the corresponding amount of calcium sulphate.

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[1] T. Engelbach, *Liebig's Ann.*, **123**. 260, 1862.

[2] R. K. Meade, *Portland Cement*, Easton, Pa., 254, 1906.

[3] The evaporation is more rapid than with clays because of the absence of large amounts of alkaline chlorides, and a smaller volume of liquid is used for the dissolution of the fused cake.

[4] Phosphatic limestones may have less alumina than is needed to combine with the phosphorus, and in that case some calcium phosphate will be precipitated with the alumina and iron hydroxide. Some, therefore, add a ferric salt to the solution before adding the ammonia, and afterwards deduct the amount of iron added from the ferric oxide obtained later—see page 606.

[5] In the case of magnesites where but little calcium and much magnesium is present, the oxalate process for lime is not suitable (F. Hundeshagen, *Zeit. öffent. Chem.*, **15**. 85, 1907). It is best to treat the filtrate—occupying, say, 30 c.c.—from the silica with 4 grms. of sodium sulphate, and 40 c.c. of 90 per cent. alcohol. After standing about five hours at 17°–20° in a covered vessel, filter the solution, and wash the precipitated calcium sulphate with 50 per cent. alcohol. In order to free the precipitate completely from magnesia, redissolve the sulphate in hot dilute hydrochloric acid, and precipitate the lime as usual by the oxalate process. The combined filtrates from the calcium sulphate and oxalate are evaporated to drive off the alcohol, the iron is oxidised with hydrogen peroxide, and aluminium and ferric hydroxides precipitated by adding ammonia. Magnesia is determined in the filtrate in the usual manner.

[6] The manganese will be found in the filtrate from the ammonia precipitate; or it may be precipitated with the alumina, etc., by adding bromine as indicated on page 177. Copper, lead, zinc, nickel (sulphides or carbonates), rare earths, chromium, vanadium, etc., are to be determined on large quantities of the sample—say 50–500 grms.

[7] As a rule, in Smith's process, about half as much calcium carbonate is needed for limestones and the more calcareous clays as is indicated in the standard directions (page 222). The precipitated calcium carbonate is much more effective in the work of decomposition than the native crystalline carbonate. If no precipitated carbonate be used, the results, with Smith's process, are usually rather low. T. Engelbach (*Liebig's Ann.*, **123**. 260, 1862) uses a modification of Berzelius' process for the alkalies in the "soluble" portion of limestones. Ignite the powdered mineral strongly over a blast, boil with a little water, filter, neutralise the solution with hydrochloric acid. Treat with ammonia and ammonium carbonate, etc. (page 226).

[8] G. Jenzsch, *Pogg. Ann.*, **96**. 145, 1855.

To get the "total sulphur," place 2 grms. of the powdered sample in a porcelain evaporating basin, and cover the mass with bromine water. Decompose the carbonates by adding 25–30 c.c. of hydrochloric acid, in small quantities at a time, to the cold solution. The "sulphide sulphur" is liberated as hydrogen sulphide, and immediately oxidised by the bromine water. If the acid be added gradually, and the bromine water be in excess, there will be no appreciable loss of sulphide. The solution is evaporated to dryness, filtered, and treated with barium chloride, etc., for barium sulphate, as indicated on page 618. The difference between the weights of barium sulphate obtained with and without the bromine water, multiplied by 0·1374, represents the corresponding amount of "sulphide sulphur."[2]

EXAMPLE.—Suppose the following results have been obtained:—

Barium sulphate (with bromine)	0·0341 grm.
Barium sulphate (without bromine)	0·0251 grm.
Barium sulphate	0·0090 grm.
Sulphide sulphur (0·0090 × 0·1374)	0·0012 grm.
Sulphur trioxide (0·0251 × 0·3430)	0·0086 grm.
Calcium sulphate (0·0251 × 0·5833)	0·0146 grm.

Sometimes the total sulphur is determined by one of the methods described on pages 621 *et seq.* Or the powdered sample can be fused with sodium carbonate and sodium nitrite (page 461).[3] Extract the mass with water. Evaporate the solution to dryness, acidify with hydrochloric acid to dryness. Boil the residue with dilute hydrochloric acid, filter, and determine the sulphates in the filtrate by the method of page 618.

Organic Matter is found in nearly all limestone rocks. Schaffgotsch's process for the determination of organic matter is to fuse, say, 5 grms. of borax glass in a platinum crucible over a Bunsen's burner[4] until the weight of the crucible and contents is constant.[5] Place 1 grm. of the sample on the borax, put the lid of the crucible in position, and fuse over the Bunsen's burner. Do not remove the lid until the contents are fused, otherwise loss by decrepitation may occur. When the evolution of gas has ceased, cool in a desiccator, and weigh. Again ignite, cool, and weigh. When the weight is constant, the difference between the weights of the crucible and contents with and without the powdered sample represents the carbon dioxide, water, and organic matter. If the carbon dioxide and water have been previously determined, the amount of organic matter follows by difference.

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[1] If phosphorus is to be determined, it is sometimes advisable to take double the amount of the sample for the operation just described, and now make the filtrate up to 100 c.c. Take 50 c.c. for the sulphur determination, and to the other 50 c.c. add 5 c.c. of nitric acid, and determine the phosphorus by Woy's process (page 595).

[2] Pyrite—FeS_2—is the commonest sulphide in limestone rocks. Some of the sulphur may come from the organic matter.

[3] A. Petzholdt, *Journ. prakt. Chem.* (1), **63**. 194, 1854; J. Roth, *ib.* (1), **58**. 84, 1853; J. J. Ebelmen, *Compt. Rend.*, **33**. 881, 1851; H. St C. Deville, *ib.*, **37**. 1001, 1853.

[4] Note, if a blast be used, the crucible and contents must be afterwards brought to constant weight over the Bunsen's burner. Borax glass can be kept in a state of fusion some 15–30 minutes without appreciable volatilisation, but there is a decided loss after a few minutes' blasting (page 578). R. Fresenius, *Zeit. anal. Chem.*, **I**. 65, 1862; A. Mitscherlich, *Journ. prakt. Chem.* (1), **83**. 485, 1861.

[5] According to O. Lutz and A. Tschischikow (*Journ. Russ. Phys. Chem. Ges.*, **36**. 1274, 1904), microcosmic salt may be used in place of borax. The salt is heated until ammonia and water have been expelled and the weight is constant. The advantage of microcosmic salt is: (1) it fuses more quickly; (2) is not so liable to loss by volatilisation. H. Rose (*Pogg. Ann.*, **116**. 131, 686, 1862; *Zeit. anal. Chem.*, **I**. 183, 1862) recommends potassium dichromate; W. Böttger (*Zeit. anal. Chem.*, **49**. 487, 1910) recommends sodium metaphosphate (see page 661); F. A. Gooch and S. B Kuzirian (*Amer. J. Science* (4), **31**. 497, 1911) recommend sodium paratungstate; and H. Rose (*Pogg. Ann.*, **116**. 635, 1862; T. W. Richards and E. H. Archibald, *Proc. Amer. Acad.*, **38**. 443, 1903) recommends silica.

Petzholdt[1] recommends the following process:—Dissolve 20 grms. of the sample in dilute hydrochloric acid, and boil the solution carefully to expel carbon dioxide. Filter any undissolved residue through ignited asbestos, and wash well with water, dry, and transfer the asbestos to a porcelain boat, which is then placed in a combustion tube charged with copper oxide (page 563) and ignited in a current of oxygen, so that the carbon dioxide can be collected in weighed potash bulb; or the carbon may be determined by the wet process (page 546).

§ 275. The Partial Analysis of Limestones, Dolomites, Magnesites, Marls, Cements, etc.

A process which occupies about three hours may now be described. The abbreviated processes are not usually quite so exact as the preceding process, but they are quite accurate enough for many purposes, particularly when a great number of analyses of one type of carbonate rock have to be made rapidly.[2] See the remarks on pages 243 and 248.

1. *Silica.*—Cautiously add 5 c.c. of concentrated hydrochloric acid to a gram of the powdered sample, keeping the basin covered during the attack by the acid so as to avoid loss by spurting. When the effervescence has ceased, evaporate the mixture to dryness.[3] Cool. Digest the residue with a little hot water and a few drops of hydrochloric acid. Heat the mixture to boiling and filter. Wash the residue on the filter paper with hot water. Ignite, and weigh as SiO_2.

2. *Alumina and Ferric Oxides.*—Precipitate the mixed ferric and aluminium hydroxides with ammonia and ammonium chloride in the usual manner (page 182), and finally weigh as $Al_2O_3 + Fe_2O_3$.

3. *Calcium Carbonate.*—Acidify the filtrate from the ammonia precipitate with hydrochloric acid. Heat the solution to boiling, and, while still boiling, gradually add, crystal by crystal,[4] approximately 3 grms. of solid oxalic acid per gram of mixed calcium and magnesium oxides.[5] When all the oxalic acid has been added, add a slight excess of ammonia. Let the solution stand until the precipitate has settled—2 or 3 minutes.[6] According to Schoch,[7] a double pre-

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[1] A. Petzholdt (*Journ. prakt. Chem.* (1), **63**. 194, 1854) considers that 58 parts of carbon correspond with 100 parts of humus. If carbon and hydrogen are both determined by combustion, 4·5 parts of hydrogen correspond with every 58 parts of carbon. The remaining hydrogen is supposed to be derived from the water. Note that hydrogen may come from the asbestos of the filter tube if the drying be imperfect, and also from the hydrated minerals. It is generally best to represent the result as "carbon derived from organic matter," without making any assumptions as to the composition of the organic matter. See page 573.

[2] K. J. Sundstrom, *Journ. Soc. Chem. Ind.*, **16**. 520, 1897; F. Hundeshagen, *Zeit. öffent. Chem.*, **15**. 85, 1909; N. Knight, *Chem. News*, **92**. 61, 108, 1905; **96**. 126, 1906; F. Clowes and J. B. Coleman, *ib.*, **92**. 259, 1905; W. H. Stanger and B. Blount, *Journ. Soc. Chem. Ind.*, **21**. 1216, 1902; Report, *ib.*, **21**. 12, 1223, 1902; G. Hentschel, *Chem. Ztg.*, **36**. 821, 1912.

[3] When the solution is evaporating, determine the mixed calcium and magnesium carbonates as described below.

[4] Otherwise loss might occur from spurting. Stir all the time the acid is being added.

[5] The magnesium must all be converted to the oxalate to prevent the solution of calcium oxalate in the magnesium chloride (page 212). The approximate amount is determined from "4" below.

[6] For more exact results, let stand overnight, or at least 3–4 hours.

[7] C. Schoch, *Die moderne Aufbereitung und Wertung der Mörtel-materialien*, Berlin, 36, 1896; W. C. Blasdale, *Journ. Amer. Chem. Soc.*, **31**. 917, 1909; E. H. Schultze, *Chem. Ztg.*,

cipitation is unnecessary; but if much magnesium be present, it is better to dissolve the washed calcium oxalate in hot hydrochloric acid, and reprecipitate by the addition of ammonia and a little ammonium oxalate to the boiling solution. Filter the calcium oxalate, and wash with cold water until the filtrate is free from chlorides and oxalates.[1] Ignite the precipitate in a platinum crucible, and finish the ignition with half an hour's blasting. Cool in a desiccator, and weigh as CaO.[2] Multiply the result by 1·7844 to get the corresponding amount of calcium carbonate.

4. *Mixed Calcium and Magnesium Carbonates.*—Weigh 1 grm. of the finely powdered sample into a small porcelain basin. Add 25 c.c. of N-HCl. Cover with a watch-glass, and, when effervescence has ceased, heat the solution to boiling. When cold, titrate the free acid with N-HaOH and with a drop of methyl orange as indicator (page 70).

Example.—One gram of limestone required 5·15 c.c. of N-sodium hydroxide for the titration after adding 25 c.c. of N-hydrochloric acid. Hence, the mixed calcium and magnesium carbonates corresponded with 19·85 c.c. of N-HCl. Again, 0·538 grm. of CaO was obtained. This corresponds with 1·7844 × 0·538 = 0·9603 grm. $CaCO_3$. But 1000 c.c. of N-HCl correspond with 28 grms. of CaO; hence, 1 grm. CaO corresponds with 35·7 c.c. of N-HCl; or 0·538 grm. CaO corresponds with 0·538 × 35·7 = 19·21 c.c. of N-HCl. Hence, 19·85 − 19·21 = 0·64 c.c. of N-HCl was needed for the magnesium carbonate. But 1 c.c. of N-HCl represents 0·042 grm. $MgCO_3$, and 0·64 c.c. corresponds with 0·042 × 0·64 = 0·0269 grm. of $MgCO_3$. Hence, the analysis reads (per cents.):

Calcium carbonate	96·03
Magnesium carbonate	2·69
Silica	1·06
Alumina and ferric oxide	0·00

The magnesium carbonate determined by this indirect process should not differ more than $\frac{1}{4}$ per cent. from that obtained by more elaborate processes.

Passon's Process for the Determination of Lime in the Presence of Alumina, etc.—If the amount of lime only is needed, Passon[3] says that calcium oxalate can be precipitated in the presence of iron, aluminium, magnesium, and phosphorus by adding a drop of phenolphthalein to the solution, and neutralising with dilute ammonia (1 : 5) until the precipitate is no longer redissolved on shaking. Add 25 c.c. of Wagner's solution.[4] If the precipitate does not all dissolve, repeat the neutralisation with ammonia. Add 12 c.c. more of Wagner's solution; dilute the solution to 200 c.c. with water. Heat the solution to boiling, and add solid ammonium oxalate until no more precipitate is produced. After standing some time (overnight), filter, wash, and ignite the calcium oxalate.[5]

Newberry's Process for the Simultaneous Determination of Magnesium and Calcium Carbonates.—Newberry[6] based a process for the volumetric determination

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29. 508, 1905; M. J. van Kruijs, *Chem. Weekblad*, **4.** 29, 1907; C. Liesse, *Ann. Chim. Anal.*, **16.** 7, 1911; B. Enright, *Journ. Amer. Chem. Soc.*, **26.** 1003, 1904; C. Stolberg, *Zeit. angew. Chem.*, **17.** 741, 769, 1904; R. F. Young and B. F. Baker, *Chem. News*, **86.** 148, 1902.

[1] Magnesium can be determined in the combined filtrates, if desired, by the method of page 218. W. F. Koppeschaar, *Zeit. anal. Chem.*, **44.** 184, 1905. The calcium oxalate can also be determined by the volumetric permanganate process (page 215). H. B. Kinnear, *Chem. Eng.*, **13.** 247, 1911.

[2] The CaO can be dissolved in 25 c.c. of N-HCl and titrated with N-NaOH in the usual manner (page 70), as a check on the weighings.

[3] M. Passon, *Zeit. angew. Chem.*, **11.** 776, 1898; **12.** 48, 1899; **14.** 285, 1901.

[4] Wagner's Solution.—Dissolve 25 grms. of citric acid and 1 grm. of salicylic acid in water, and make the solution up to a litre.

[5] R. K. Meade (*Chem. Eng.*, **1.** 21, 1905; *Portland Cement*, Easton, Pa., 189, 1906) and K. Balthaser (*Chem. Ztg.*, **33.** 646, 1909) describe volumetric processes for the determination of lime without the separation of silica, etc.

[6] S. B. Newberry, *Cement Eng. News*, **15.** 35, 1903; *Tonind. Ztg.*, **27.** 833, 1903.

of calcium and magnesium carbonates on the fact that magnesium hydroxide is sufficiently soluble in water to colour phenolphthalein; and when boiled with a dilute solution of sodium hydroxide, the magnesium is completely precipitated and separated from the calcium.

Dissolve half a gram of limestone in an Erlenmeyer's flask fitted with a long "condenser tube" (fig. 185, page 582) to serve as condenser. Add 60 c.c. of $\frac{1}{5}$N-hydrochloric acid ("first acid"),[1] and boil the solution for 2 minutes with the condenser tube in position. Wash the interior of the condenser tube into the flask by means of a wash-bottle. Remove the tube and cool the solution thoroughly in the cooling-box (page 72). Add 5 drops of phenolphthalein solution and titrate with $\frac{1}{5}$ N-sodium hydroxide ("first alkali") until a faint pink colour appears in the solution. This may fade in a few seconds.[2]

Transfer the neutral solution to a large test tube (12 inches long and 1 inch internal diameter) provided with a mark[3] corresponding with 100 c.c. Heat the solution to boiling, add $\frac{1}{5}$N-NaOH, $\frac{1}{2}$ c.c. at a time, and boil after each addition. When a deep red colour is obtained which does not become paler on boiling, read the burette ("second alkali"). Dilute the solution to 100 c.c.; boil for a moment; and let the precipitate settle. When the precipitate has settled, pipette 50 c.c. of the clear solution into a flask and titrate with $\frac{1}{5}$N-HCl until the pink colour has gone ("second acid").[4]

Example of Calculation.—Suppose 11·6 c.c. alkali ("first alkali") were needed for the first titration, cold; and 3·55 c.c. of alkali ("second alkali") were needed for the second titration, hot. Suppose, further, that 50 c.c. of the solution required 0·45 c.c. of acid for decolorisation ("second acid"). Then,

$$(\text{Second alkali} - \text{second acid})2 \times 0{\cdot}84 = 1{\cdot}68(3{\cdot}55 - 0{\cdot}90)$$
$$= 4{\cdot}45 \text{ per cent. of magnesium carbonate.}$$
$$\{\text{First acid} - (\text{First alkali} + \text{second alkali} - \text{second acid})\}2 \times 1{\cdot}00$$
$$= 2\{60 - (11{\cdot}60 + 3{\cdot}55 - 0{\cdot}90)\}$$
$$= 91{\cdot}50 \text{ per cent. of calcium carbonate.}$$

If the results are to be expressed in terms of MgO and CaO, substitute 0·40 for 0·84, and 0·56 for 1·00, in the preceding formulæ.

The results for magnesium carbonate are usually a little low, and for lime a little too high. This is probably due to the formation of calcium carbonate by the absorption of carbon dioxide of the air during the precipitation of magnesia, and to the insolubility of the lime compounds in the sample. If much soluble alumina and iron be present, the end point is obscured and the readings are more difficult. With the high-grade limestones the results are suitable for technical work. With marble containing 54·62 per cent. CaO and 0·84 per cent. MgO by the gravimetric process, 54·99 and 0·88 respectively were obtained by Newberry's process. With a magnesian marl containing 5·43 per cent. of alumina and ferric oxide, 52·08 per cent. of silica, 19·52 per cent. of CaO, and 2·24 per cent. of magnesia, Newberry's process gave:

CaO	17·02	16·83	17·36	per cent.
MgO	2·08	2·30	2·00	per cent.

A sample of dolomitic marl with 26·50 per cent. CaO and 18·76 MgO:

CaO	26·38	25·42	25·53	per cent.
MgO	17·80	18·40	18·96	per cent.

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[1] Standardised against Iceland spar.

[2] If the titration be carried until a permanent red coloration appears, the lime will be too low. If the limestone under investigation contains inappreciable amounts of magnesia, this completes the determination: (first acid − first alkali) × 2 × 0·56 = the per cent. of CaO.

[3] A band of paper or etched ring.

[4] If more than 1 c.c. of acid be required, too much alkali was added, and the magnesium hydroxide will have carried down some $Ca(OH)_2$.

were obtained. Experiments with artificial mixtures of Iceland spar and magnesium carbonate gave excellent results. The results with the less pure limestones and calcareous marls are not so good.

Magnesite.—In the case of magnesites,[1] the joint magnesia and lime[2] may be determined by boiling 0·5 grm. of the magnesite with a known excess of standard sulphuric acid and titrating back the excess with standard sodium hydroxide. The lime can be precipitated from the solution by adding an excess of 90 per cent. alcohol—250 c.c. of alcohol per 100 c.c. of the solution. Let the mixture stand in a covered vessel overnight. Filter and wash with 50 per cent. alcohol, and proceed as indicated in the footnote, page 212. After subtracting the calcium oxide from the joint magnesium and calcium oxides obtained by the titration, the amount of magnesia follows at once. The magnesia may exist in the form of oxide, hydroxide, or carbonate.[3] The hydroxide can be determined from the loss in weight which occurs when the sample is baked to a constant weight at 300°–350°, and the carbonate from the loss in weight which occurs when the same sample is calcined to constant weight at a red heat. The difference between the amounts so determined and the total magnesia represents the magnesium oxide. Of course, the water and carbon dioxide can be determined by the more laborious processes, pages 559 *et seq.*[4] The value of burnt magnesite depends upon the proportion of "active magnesia." The "active magnesia" is the difference between the total magnesia, MgO, and that combined with carbon dioxide and water.[5]

§ 276. The Mineralogical Analysis of Limestones and Marls.

Calcium carbonate is undoubtedly the prevailing constituent of limestone rocks, and magnesium carbonate is probably next in importance. With increasing proportions of the latter, the carbonate rock passes into dolomite, magnesian limestone, and finally magnesite. Ferrous and manganese carbonates are probably present in small quantities, and when these compounds predominate, siderite and other ores of iron and manganese result. It is usual, in technical analyses, to report the lime and magnesia as carbonates, and the iron and manganese as oxides. In all probability, the two latter more generally exist as carbonates. A determination of the carbon dioxide will sometimes show that more carbon dioxide is present than is required for the lime and magnesia. Some of the lime and magnesia may also be combined with the silica and alumina, and, in consequence, even if the amount of carbon dioxide does satisfy the lime and magnesia, some may be combined with the iron and manganese. Phosphorus may be combined with the iron and aluminium, or be present as apatite, etc. The silicate minerals associated with the calcareous clays and limestones are probably as varied as the silicate minerals found in clays (*q.v.*).[1]

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[1] For volumetric process, *Chem. Ztg.*, **33**. 545, 1909.

[2] If the amount of calcium relatively with the magnesium is very small, O. Kallauner and I. Preller (*Chem. Ztg.*, **36**. 449, 462, 1912) show that the oxalate process (pages 212–3) is trustworthy only if dilute solutions are used, and if a large excess of ammonium salts and ammonium oxalate are present, and if the solution is filtered immediately after precipitation; or if the precipitation is repeated: otherwise the lime is always 0·15 to 0·2 per cent. low, owing to resolution during washing. Most methods involving the precipitation of calcium sulphate in alcoholic solutions are unreliable if much magnesia is present. Good results are obtained as follows: (1) Precipitate the lime as oxalate, filter and wash, convert the oxalate into sulphate, dissolve the sulphate in hydrochloric acid, reprecipitate as oxalate, and weigh as CaO. Or (2), evaporate a solution of the mixed chlorides to dryness with lithium sulphate, treat the residue with a mixture of 10 volumes of ethyl alcohol with 90 volumes of methyl alcohol saturated with lithium sulphate. The precipitated calcium sulphate is dissolved in hydrochloric acid and reprecipitated by the oxalate process—E. C. Carron, *Ann. Chim. Anal.*, **17**. 127, 1912.

[3] For the total magnesia in magnesites, J. Mayrhoffer (*Zeit. angew. Chem.*, **21**. 592, 1908) decomposes 5 grms. of the finely powdered mineral with aqua regia on a water bath. Evaporate the solution to dryness to render the silica insoluble. Digest with acidulated water, filter, and make the solution up to a litre; mix 40 c.c. (20 c.c. if burnt magnesite is in question) with 5 c.c. of sulphuric acid and 100 c.c. of citrate solution (100 grms. citric acid, 333 c.c. of ammonia—sp. gr. 0·91—made up to a litre with water), 20 c.c. of a 10 per cent. solution of disodium hydrogen phosphate, and 15 c.c. of ammonia. Stir the mixture 5 minutes without touching the walls of the beaker. Filter, etc., after standing 5 minutes. The calcium is not precipitated in presence of the ammonium citrate.

[4] For the determination of magnesia in the presence of magnesium carbonate from the heat of the reaction with hydrochloric acid, see V. Fortini, *Chem. Ztg.*, **36**. 270, 1912.

[5] O. Kallauner, *Chem. Ztg.*, **36**. 711, 1912; L. Dede.

Many attempts have been made to isolate the different minerals in limestones and marls by treatment with different solvents. Struckmann[2] analysed various marls by digesting the samples first with water, then with acetic acid, and finally with hydrochloric acid. Each solution and the residue was examined separately. Bolton[3] studied the action of citric and tartaric acids, and Jannettaz,[4] the action of potassium bisulphate. Deville[5] tried to dissolve calcium carbonate from mortars by boiling the mixture with a solution of ammonium nitrate, which he supposed did not attack the silicates; but Gunning showed that Deville's assumption is faulty. Browne and Harrison's[6] method of dealing with the problem is as follows:—

Clay and Quartz.—Digest 5 grms. of the dried (air) and powdered sample in dilute hydrochloric acid (2·5 per cent.)[7] in the cold (30°). When effervescence has ceased, decant the solution through a filter paper. Heat the residue on a water bath several hours with a concentrated solution of sodium carbonate containing some sodium hydroxide,[8] and wash the residue at the filter pump (1) with the same solution; (2) with water; and (3) with dilute hydrochloric acid. Ignite, and weigh the residue as "clay and siliceous minerals."

Reduce the residue to an impalpable powder in an agate mortar, and boil a weighed portion repeatedly with concentrated sulphuric acid until the clay is quite decomposed. Drive off the excess of acid, and heat the residue with dilute hydrochloric acid to dissolve basic aluminium and ferric sulphates. Heat the residue with the sodium carbonate solution to dissolve the silica set free during the decomposition of the clay. The final residue represents the crystalline siliceous minerals, mostly quartz. The difference between this result and the preceding, multiplied by 1·164, represents the amount of clay, provided it be assumed that the clay can be represented by $Al_2O_3.2SiO_2.2H_2O$, and that ignited clay is all dissolved by the treatment in question. For the limitations involved in the assumption see pages 661 *et seq.*

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[1] W. F. Hume, *Chemical and Mineralogical Researches on the Upper Cretaceous Zones of the South of England*, London, 1893; S. Pfaff, *Ueber die unlöslichen Bestandtheile der Kalk und Dolomite*, Halle, 1878; L. Cayeux, *Ann. Soc. Géol. du Nord*, **16**. 342, 1890; A. Vesterberg, *Bull. Geol. Inst. Upsala*, **5**. 97, 1900; **6**. 254, 1904; K. Haushofer, *Sitzber. K.K. Akad. Wiss. München*, **11**. 220, 1881.

[2] C. Struckmann, *Liebig's Ann.*, **74**. 170, 1858; C. J. B. Karsten, *Archiv Min.*, **22**. 592, 607, 613, 1848; E. Damour, *Bull. Soc. Geol.* (2), **6**. 313, 1849; G. Forchhammer, *Journ. prakt. Chem.* (1), **49**. 55, 1850; J. Roth, *Zeit. deut. geol. Ges.*, **4**. 565, 1852; T. Liebe, *ib.*, **7**. 406, 1855; F. Hoppe-Seyler, *ib.*, **27**. 499, 1875; F. Pfaff, *Pogg. Ann.*, **82**. 488, 1851; T. S. Hunt, *Amer. J. Science* (2), **28**. 181, 371, 1859; M. Schafhäutl, *Neues Jahrb. Min.*, 812, 1864; C. Knausz, *Chem. Centr.* (1), **26**. 244, 1855; C. Doelter and R. Hörnes, *Jahrb. geol. Reichsanst.*, 69, 1875; C. Schmidt, *N. Petersb. Acad. Bull.*, **16**. 205, 1871.

[3] H. C. Bolton, *Ann. N.Y. Acad. Science*, **1**. 1, 153, 1877-80; *Proc. Amer. Assoc. Adv. Science*, **31**. 271, 1883; *Chem. News*, **36**. 249, 1877; **37**. 14, 24, 65, 86, 98, 1878; **38**. 168, 1878; **43**. 31, 39, 1881; **47**. 251, 1883; J. W. Richards and N. S. Powell, *Journ. Amer. Chem. Soc.*, **22**. 117, 1900.

[4] E. Jannettaz, *Compt. Rend.*, **77**. 838, 1873; **78**. 852, 1874.

[5] H. St C. Deville, *Compt. Rend.*, **37**. 1001, 1853; J. W. Gunning, *Journ prakt. Chem.*, (1), **62**. 318, 1854.

[6] A. J. J. Browne and J. B. Harrison, "On the Geology of Barbados," *Journ. Geol. Soc.*, **48**. 170, 1892.

[7] Dilute acetic acid was tried, but it only partially attacked the zeolites, and the silica set free from these minerals was estimated as colloidal silica.

[8] LUNGE'S SOLUTION.—Dissolve 100 grms. of crystalline sodium carbonate and 10 grms. of sodium hydroxide in water, and make the solution up to a litre with water. Remember that the solution will take silica from the glass of the bottle if it be stored in glass bottles.

Colloidal Silica.—Treat 5 grms. of the (air) dried and powdered sample in dilute hydrochloric acid (2·5 per cent.) in the cold (30°). Evaporate the solution to dryness in a porcelain basin, with the usual precautions against loss by spurting (page 167), in order to render the silica insoluble Digest the residue in warm hydrochloric acid, add water, filter and wash. Ignite the residue and weigh. The insoluble matter consists of the residue insoluble in dilute hydrochloric acid, together with the colloidal silica originally present in the sample, and that formed by the decomposition of certain hydrated silicates and aluminium silicate, which might be present in small quantities. The difference between the weight of this mixture and the "clay and quartz" resulting from the preceding operation represents the colloidal silica.[1]

Example.—Suppose that 5 grms. of gault clay furnished :

Clay and quartz residue	0·2514 grm.
Quartz residue	0·1255 grm.
Calcined clay	0·1259 grm.
Siliceous residue	0·3819 grm.
Clay and quartz residue	0·2514 grm.
Colloidal silica	0·1305 grm.

The calcined clay corresponds with 0·1259 × 1·164 = 0·1465 grm. of clay. Hence, the sample would be reported to contain :

Quartz residue	2·51 per cent.
Clay residue	2·93 per cent.
Colloidal silica	2·61 per cent.

Alumina, ferric oxide, etc., can be determined in the filtrate from the silica in the usual manner.

For the determination of sand, see "Elutriation" in the second volume of this work.[2]

Clay in Limestones.—A number is obtained by the following process which is generally supposed to represent the amount of "clay" in the given limestone :—Digest 2 grms. of the powdered sample with 40 c.c. of water and 4 c.c. of concentrated hydrochloric acid as indicated on page 525. When effervescence has ceased, boil the solution for about 10 minutes to drive off the carbon dioxide. Precipitate any iron and aluminium which may have gone into solution by the addition of ammonia. Filter through a Gooch's crucible, wash, and ignite at a low red heat. Between one and two hours are required for the determination. Archetti[3] considers that, if much magnesia be present, the results will be high, because some magnesium hydroxide will be precipitated by the ammonia. In that case, consequently, Archetti prefers to treat 2 grms. of the sample with 10 per cent. hydrochloric acid mixed with $\frac{1}{10}$th its volume of 10 per cent. nitric acid. When solution is complete, add an excess of ammonium chloride and a slight excess of ammonia. Wash the precipitate, etc., as before.

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[1] The term "colloidal silica" is here synonymous with "silica soluble in dilute hydrochloric acid."

[2] Note that burnt limestones and burnt magnesites may contain more "soluble silica" than the raw material, owing to the formation, during calcination, of silicates, which can be decomposed by treatment with acids.

[3] A. Archetti, *Bull. Chim. Pharm.*, 48. 409, 1909.

§ 277. The Determination of Free Lime in Quicklime, Mortars, etc.

Free lime may be detected in whiting by boiling a couple of grams for about 5 minutes with 100 c.c. of water. An alkaline reaction—development of a red colour with phenolphthalein—is generally taken to represent free lime, although, of course, the coloration may possibly be due to the partial hydrolysis of the carbonate, and to the presence of alkaline hydroxides, or carbonates in the original sample.

Winkler's Process.—To determine the free lime in quicklime,[1] carefully slake 10 grms. of the sample with water, and transfer the resulting cream to a 250-c.c. flask and make the contents up to the mark with distilled water. Pipette 25 c.c. (=1 grm. of the sample) of the thoroughly mixed contents into an Erlenmeyer's flask; add a few drops of phenolphthalein[2] as indicator, and titrate slowly with N-hydrochloric acid until the red colour disappears. The colour change takes place before the calcium carbonate is attacked by the acid, and it is possible to strike the point where all the calcium hydroxide is just neutralised. The small amount of carbon dioxide liberated by the next drop or two of the standard acid decolorises the phenolphthalein, and indicates the end of the titration. The acid must be added very slowly with constant stirring to get reliable results.

Stone and Schenck's Process.[3]—This is based on the fact that calcium oxide forms soluble compounds with a solution of sugar under conditions where calcium carbonate, alumina, and ferric oxides remain unaffected. Hence, shake, say, 1 grm. of the powdered sample with 500 c.c. of a 10 per cent. solution of cane sugar for 20 minutes. Filter, and wash with the solution of sugar. The lime in the filtrate can be determined either by precipitation as calcium oxalate, or volumetrically by titration with standard hydrochloric acid. The authors say that "magnesia is not soluble to any appreciable extent in the solution of cane sugar containing lime, under the stated conditions."

Frühling's Method.[4]—5 grms. of the powdered sample are introduced into a stoppered Erlenmeyer's flask. Add 100–150 c.c. of water, and 30 drops of phenolphthalein solution. Shake the contents thoroughly. Wash the sides of the flask and the stopper. Add, say, 30 c.c. of standard hydrochloric acid[5] from a burette. The red colour of the solution may disappear, but it will reappear if the flask be agitated, because "quicklime" generally contains more than 60 per cent. of CaO. Add a gram of ammonium chloride. The remaining calcium hydroxide decomposes the ammonium salt, liberating an equivalent amount of ammonia. This facilitates subsequent titration. Add the hydrochloric acid 1 c.c. at a time until the red colour no longer reappears when the flask is agitated. As soon as the red colour takes an appreciable time to return, the acid is added 0·1 c.c. at a time. If the red colour does not appear after the agitated solution has stood 5 minutes, read the volume of acid used, multiply the result by 2 to get the corresponding amount of CaO in the given sample. For instance, if 38 c.c. of hydrochloric acid had been employed, the sample contained 76 per cent. of CaO. Frühling's process is also applied to the determination of lime in mortar.[1] The mortar is well mixed by passing it through a sieve with a stiff brush. Weigh 100 grms.[2] into a stoppered flask. Add 25 grms. of ammonium chloride, 100 c.c. of water, and 20 drops of phenolphthalein. Add 50 c.c. of the standard hydrochloric acid. The red colour disappears temporarily, but reappears on shaking. This shows that free lime is still present. Continue adding acid 1 c.c. at a time, until the red colour reappears but slowly. Then add the acid in smaller portions at a time, say 0·5 c.c. Finally, when the red colour does not appear until the solution has stood for 5 minutes, the titration is complete, and the calculation is made as before.[3]

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[1] Also, of course, in slaked lime. A. Winkler, *Journ. prakt. Chem.* (1), **67**. 444, 1856; W. Richter, *Tonind. Ztg.*, **27**. 1862, 1943, 1903.

[2] A. Gawalovski, *Zeit. anal. Chem.*, **22**. 397, 1883; F. W. Küster, *Zeit. anorg. Chem.*, **13**. 141, 1897; G. Lunge, *Zeit. angew. Chem.*, **10**. 41, 1897; C. Winkler, *Praktische Uebungen in der Maassanalyse*, Leipzig, 1888. For phenacetolin as indicator, see page 63.

[3] W. E. Stone and F. C. Schenck, *Journ. Amer. Chem. Soc.*, **16**. 721, 1894; *Chem. News*, **70**. 278, 1894; J. Hendrick, *Analyst*, **32**. 320, 1907. For the solubility of lime in saccharine solutions, see J. Weisberg, *Bull. Soc. Chim.* (3), **21**. 773, 1899; **23**. 740, 1900; *Chem. News*, **82**. 284, 1900. See also W. Heldt, *Journ. prakt. Chem.* (1), **94**. 129, 1865; L. C. Levoir, *Rec. Travs. Pays-Bas*, **5**. 59, 1886; C. Parsons, *Deut. Töp. Zeig. Ztg.*, **2**. 585, 1888; W. P. Mason, *Journ. Amer. Chem. Soc.*, **16**. 733, 1894; O. Rebbufat, *Tonind. Ztg.*, **23**. 782, 823, 883, 900, 1899; *Gazz. Chim. Ital.*, **28**. ii, 209, 1899.

[4] R. Frühling, *Tonind. Ztg.*, **8**. 393, 1884; H. Seger and E. Cramer, *ib.*, **31**. 619, 1907.

[5] 1000 c.c. of the hydrochloric acid have 130·3 grms. of HCl, and this is equivalent to 100 grms. of CaO. Hence, 1 c.c. of the standard solution corresponds with 0·1 grm. of CaO.

Estimates of the free lime in cements are now seldom published in technical papers, because no method is yet known which will give satisfactory results. Some of the calcium silicates and aluminates are decomposed, by hydrolysis, at the same time as the "free lime" is dissolved. Solutions of glycerol[4] in water; iodine solutions;[5] dilute hydrochloric acid;[6] ammonium salts (page 525);[7] etc.,[8] have been proposed and found unsatisfactory. The same might be stated concerning the attempt to determine this constant from the amount of "heat" developed during hydration.[1]

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[1] M. Holmblad, *Tonind. Ztg.*, **13**. 143, 1889; H. Seger and E. Cramer, *ib.*, **26**. 1719, 1902.

[2] A small brass cylinder, closed at one end, and fitted with a movable piston, is sometimes used when the mortar is evaluated by volume, not by weight. The cylinder holds 50 c.c. of mortar, and it is filled by placing the mouth of the cylinder with the piston depressed into the mass of mortar. By elevating the piston, and pressing the cylinder into the mortar, the latter is easily filled. By depressing the piston, 50 c.c. of mortar can be delivered into the glass cylinder for analysis. The final result is then represented as kilograms (or lbs.) per cubic metre (or cubic foot).

[3] If the sand mixed with the lime contains calcium carbonate, the lime content of the mortar may come out too high, because some of the acid may have attacked the carbonate. The calcium hydroxide is, however, attacked before the carbonate, as indicated under "Winkler's process," above. See H. E. Kiefer, *Journ. Ind. Eng. Chem.*, **4**. 358, 1912; A. H. White, *ib.*, **1**. 6, 1909.

[4] F. Hart, *ib.*, **24**. 1674, 1900; M. Mayard, *Bull. Soc. Chim.* (3), **27**. 851, 1902; *Chem. News*, **87**. 109, 1903.

[5] F. Hart, *Dingler's Journ.*, **175**. 208, 1865.

[6] C. Zulkowsky, *Tonind. Ztg.*, **22**. 285, 1898; H. Hauenschild, *ib.*, **19**. 239, 1895; E. Fremy, *Compt. Rend*, **67**. 1205, 1868; E. Laudrin, *ib.*, **96**. 156, 379, 841, 1229, 1883; F. Schott, *Dingler's Journ.*, **202**. 434, 1871; G. Feichtinger, *ib.*, **174**. 437, 1864; A. Schulatschenko, *ib.*, **194**. 355, 1869.

[7] G. Berju and W. Kosinenko (*Landw. Ver. Stat.*, **60**. 419, 1904; A. Bodenbender and E. Ihlee, *Zeit. Ver. Rübenzuckerind.*, **29**. 714, 1907) use ammonium nitrite; M. Heyer (*Chem. Ztg.*, **33**. 102, 1157, 1909; P. Philossophoff, *ib.*, **33**. 67, 1909; M. Popel, *Zeit. angew. Chem.*, **21**. 2080, 1908; F. Knapp, *Dingler's Journ.*, **265**. 184, 1887; M. Tomëi, *Tonind. Ztg.*, **19**. 177, 1895; H. Hauenschild, *ib.*, **19**. 239, 1895; S. Wormser, *ib.*, **24**. 1636, 2072, 1900; E. Michel, *Journ. prakt. Chem.* (1), **33**. 548, 1844) uses ammonium chloride; R. Brandenberg (*Chem. Ztg.*, **33**. 880, 1909) distils with an alcoholic solution of ammonium bromide. The ammonia in the distillate corresponds with the calcium oxide. J. Hendrich (*Journ. Soc. Chem. Ind.*, **28**. 775, 1909; **30**. 520, 1911) determined the free lime in basic slags by distilling them with solutions of ammonium sulphate and chloride, and estimated the basicity of the slag from the amount of ammonia given off: $(NH_4)_2SO_4 + CaO = CaSO_4 + H_2O + 2NH_3$. The ammonia evolved owing to the hydrolysis of the ammonium salts (W. Smith, *Journ. Soc. Chem. Ind.*, **15**. 3, 1896; **30**. 253, 1911; V. H. Veley, *Journ. Chem. Soc.*, **87**. 26, 1905) is negligibly small, and he claims the results are satisfactory. G. Feichtinger (*Bayer. Kunst. Gewerb.*, 69, 1858) used ammonium carbonate; M. Tomëi (*Tonind. Ztg.*, **19**. 177, 1895) used ammonium hydroxide, and also ammonium acetate; S. Wormser (*Tonind. Ztg.*, **24**. 28, 1900) ammonium oxalate; C. Winkler (*Dingler's Journ.*, **175**. 208, 1865).

[8] M. Bischoff (*Chem. Ztg.*, **29**. 82, 1903) recommends water for extracting lime from slags, since he thinks sugar solutions dissolve calcium hydrogen carbonate. E. H. Keiser and S. W. Forder (*Amer. Chem. Journ.*, **31**. 153, 1904) propose to determine lime in commercial quicklime, slags, and cements by digesting with water—free lime is attacked at once, calcium silicates but

§ 278. The Analysis of Calcium Sulphate, Plaster of Paris, and Gypsum.

Gypsum, terra alba, plaster of Paris are more or less pure varieties of calcium sulphate. The analysis of calcium sulphate generally involves the determination of lime (CaO), sulphur trioxide (SO_3), water, silica, iron, aluminium oxides, magnesia, and carbon dioxide.[2] Calcining and physical tests show value of gypsum and plaster of Paris better than chemical analysis. For the loss of moisture when grinding the sample, see page 124.

Moisture.—Heat about a gram of the sample one hour at 105°, and note the loss in weight.[3] Heat a weighed amount of the sample (say, 1 grm.) in a crucible on a hot plate, and finally at a dull red heat, over a Bunsen's burner for about 10 minutes, and at a rather lower temperature for about 40 minutes. Cool and weigh. Repeat the ignition until a constant weight is obtained. This gives the total water.

EXAMPLE.—Suppose that:

Crucible and 1 grm. of raw gypsum	20·2682	grms.
Crucible and gypsum at 105° (1 hr.)	20·1114	,,
Crucible and gypsum at 105° (½ hr. more)	20·1113	,,
Water lost at 105°	0·1569	grm.
Crucible and raw gypsum	20·2682	grms.
Crucible and gypsum at dull redness	20·0592	,,
Total water	0·2090	grm.
Water lost at 105°	15·69	per cent.
Total combined water	20·90	,,

Frey's Process for the Different Forms of Plaster.—In view of the different forms of plaster on the market, it is required to determine the different modifications[4] of plaster in a given sample. The problem, at present, has not been solved completely, but Frey[5] has made the best attempt. The hemihydrate—$CaSO_4 \cdot \frac{1}{2}H_2O$—is estimated by finding the amount of water taken up at ordinary temperatures, and retained at 60°. 5 grms. of the sample are spread in

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slowly (C. Winkler, *Chem. Centr.* (2), **3**. 482, 1858; H. le Chatelier, *Bull. Soc. Chim.* (2), **41**. 377, 1884; L. C. Levoir, *Rec. Travs. Pays-Bas*, **5**. 59, 1886; C. Zulkowsky, *Chem. Ind.*, **24**. 290, 1901); water and carbon dioxide (G. Feichtinger, *Dingler's Journ.*, **174**. 437, 1864; C. Winkler, *l.c.*; L. C. Levoir, *l.c.*); limewater (E. Laudrin, *l.c.*; H. le Chatelier, *l.c.*); sodium carbonate (G. Feichtinger, *Bayer. Kunst. Gewerb.*, 69, 1858; F. Schott, *Dingler's Journ.*, **202**. 434, 1871); potassium carbonate (G. Oddo and E. Manselle, *Gazz. Chim. Ital.*, **25**. ii, 101, 1895; G. Feichtinger, *l.c.*); sodium hydroxide (F. Hart, *Tonind. Ztg.*, **24**. 1674, 1900); magnesium chloride (F. Knapp, *Dingler's Journ.*, **265**. 184, 1887); magnesium nitrate (C. Zulkowsky, *Zeit. Niederösterreich Ing. Ver.*, 1863); calcium chloride (L. C. Levoir, *Rec. Travs. Pays-Bas*, **3**. 55, 1885); aluminium chloride (S. Wormser and O. Spanjer, *Tonind. Ztg.*, **23**. 1785, 1899); water glass (W. Heldt, *Journ. prakt. Chem.* (1), **94**. 129, 1865); hydrogen sulphide (B. Steuer, *Tonind. Ztg.*, **23**. 1604, 1899).

[1] W. Ostwald and R. Blank, *Riga. Ind. Ztg.*, **9**., 208, 1883.

[2] E. H. S. Bailey, *Univ. Geol. Sur. Kansas*, **5**. 166, 1899.

[3] Gypsum—$CaSO_4 \cdot 2H_2O$—commences to lose water when heated to 80°, and all is driven off at about 300°. Three-fourths of the water is driven off at 160°, and the remainder at 400°. Gypsum heated to about 400° forms "dead burnt" and flooring plaster. V. Zunino, *Gaz. Chim. Ital.*, **30**. i. 333, 1910. G. Surr (*Eng. Min. World*, **36**. 467, 1912) recommends reporting as "moisture" the loss of weight gypsum suffers on heating to 80°, and "combined water" at 200°.

[4] For the five different modifications, see J. H. van't Hoff, *Zeit. phys. Chem.*, **45**. 257, 1903; P. Rohland, *Zeit. anorg. Chem.*, **35**. 201, 1903; **36**. 332, 1903.

[5] O. Frey, *Tonind. Ztg.*, **33**. 1229, 1909.

a thin layer over a porcelain basin, and just covered with water from a wash-bottle. In 30 minutes, the basin is placed in a drying oven at 60°, and kept at that temperature until the weight is constant. If a grms. of water are taken up, the weight y of hemihydrate in the sample is

$$y = 5{\cdot}37a \qquad (1)$$

unless soluble anhydrite be also present. In that case, the weight of the anhydrite z must be taken into account from (3) below:

$$y = 5{\cdot}37(a - 0{\cdot}26z) \qquad (2)$$

The soluble anhydrite is estimated by exposing 5 grms. of the sample in a thin layer as before to water vapour at the ordinary temperature for a period of 7 days under a bell-jar. The whole of the soluble anhydrite is thus converted into hemihydrate, and if b represents the increase in weight after drying at 60°–70°,

$$z = 15{\cdot}11b \qquad (3)$$

To detect soluble anhydrite, a portion of the plaster is lawned into a small cylinder containing 200 c.c. of water in which a sensitive thermometer is immersed. If soluble anhydrite be present, the temperature rises almost at once, and continues to rise for about 2 minutes. The rise of temperature which occurs when the hemihydrate is alone present begins some 5 minutes after the mixing, and continues rising for about 20 minutes.

The proportion of flooring plaster[1] found in plaster of Paris which has been burnt at too high a temperature is estimated by wetting 5 grms. as in the estimating of the hemihydrate, allowing it to remain 7 days in a moist atmosphere, and finally drying at 60°. If c denotes the increase in weight, the amount e of the flooring plaster is

$$e = 3{\cdot}78(c - a) \qquad (4)$$

The constituents indicated above are all capable of hydration, but, in addition to these active components, the sample may contain unburnt gypsum, dead-burnt plaster, natural anhydrite, and impurities—clay and sand. The unburnt plaster is estimated by finding the loss in weight on ignition. If the loss in weight be w, the weight of unburnt gypsum r is

$$r = 4{\cdot}78(w - 0{\cdot}062y) \qquad (5)$$

The total calcium sulphate as determined from the weight of the sulphate present is S. The weight t of natural anhydrite and of dead-burnt plaster is then

$$t = S - (0{\cdot}93y + z + e + 0{\cdot}79r) \qquad (6)$$

The sand and clay are determined by difference.

Silica.—Digest 1 grm. of the powdered sample in an evaporating basin with 20 c.c. of concentrated hydrochloric acid and 20 c.c. of water. Evaporate the solution to dryness. Boil the mass several times[2] with 100 c.c. of dilute hydrochloric acid (1 : 3). Filter, and collect the insoluble matter on a filter paper, wash with hot water, ignite, weigh, and report as insoluble siliceous minerals, or treat the residue as in clay analysis with hydrofluoric acid.[1]

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[1] Flooring or hydraulic plaster—*Estrichgips*—is gypsum which has been calcined at about 400°, and which has accordingly lost all its water, but, unlike "dead-burnt plaster," is able to combine with water to form a cement. Flooring plaster and dead-burnt plaster are both dehydrated, but the former is active and admits of rehydration, the latter is inactive. J. H. van't Hoff and J. Just, *Sitzber. K. Preuss. Akad. Wiss.*, I. 249, 1903.

[2] A single boiling may not suffice to dissolve all the calcium sulphate. There is here a danger of error owing to some calcium sulphate escaping solution.

Alumina and Ferric Oxide.—Make the filtrate to 500 c.c. in a measuring flask. Transfer 300 c.c. to a 600-c.c. Erlenmeyer's flask. Precipitate the ferric and aluminium hydroxides with ammonia, ignite the washed precipitate with the residue left after treating the siliceous residue with hydrofluoric acid.

Lime and Magnesia.—The filtrate from the ammonia precipitate is concentrated by evaporation, and the lime and magnesia determined in the usual manner (pages 213 and 218).

Sulphuric Acid.—The 200 c.c. remaining in the measuring flask are treated with barium chloride as described on page 618. The amount of barium sulphate, multiplied by 0·5833, represents the corresponding amount of calcium sulphate; and by 0·2402 gives the corresponding amount of CaO. If the amount of CaO so determined is less than the amount obtained by the oxalate process, the remaining CaO will probably have been combined with carbon dioxide; and the amount of calcium carbonate is determined by multiplying the difference between the two results by 1·7844. Carbon dioxide is not usually present. If it is, the amount can be determined by the process described on page 552.

EXAMPLE.—Suppose that the analysis of a sample of gypsum furnished:

Barium sulphate	1·3156 grm.
Calcium oxide	0·3295 grm.

Hence, 1·3156 × 0·2402 = 0·3160 grm. CaO; and 0·3295 less 0·3160 = 0·0135 grm. CaO. Consequently, the sample has 0·0135 × 1·7844 = 0·0240 grm. $CaCO_3$; and 1·3156 × 0·5833 = 0·7674 grm. $CaSO_4$.

§ 279. The Analysis of Barytes and Witherite.

Barytes, heavy spar, or barite is a variety of native barium sulphate; and witherite a native barium carbonate. These minerals are so cheap that they are very seldom adulterated, and the analysis is therefore directed to the determination of the natural impurities.[2] The minerals are often found in commerce ground to impalpable powders. The analysis may involve the determination of barium and calcium sulphates, barium and calcium carbonates, magnesia, silica, alumina, ferric oxide, and moisture. This latter is determined by drying about 2 grms. at 110° for a couple of hours. Traces of lead, and copper sulphides, zinc, are sometimes present. Fluorides (fluorspar) are not at all uncommon. A high-grade sample may run:

$BaSO_4$.	SiO_2.	Al_2O_3.	Fe_2O_3.	$MgCO_3$.	$CaCO_3$.	H_2O.
96·5	0·5	0·5	0·2	0·2	1·2	0·5

Barium Sulphate and Silica.—Boil a gram of the sample in dilute hydrochloric acid (1 : 3), and evaporate the solution to dryness. Moisten the mass with dilute acid, digest with water, boil, filter, wash. The filtrate contains free iron oxide, alumina, magnesia, etc.;[3] the insoluble residue contains barium sulphate and "silica." Ignite and weigh in a platinum crucible[4] as "total insoluble."[5] This is sometimes reckoned as barium sulphate. To correct the

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[1] Or fuse the residue with sodium carbonate; digest with hydrochloric acid; evaporate to dryness for silica; digest the dry mass with dilute hydrochloric acid; filter; wash; and add the filtrate to the main solution.

[2] J. Aron, *Notizblatt*, 8. 293, 1872.

[3] Barium carbonate, if present, is also dissolved. The barium chloride can be removed from the filtrate by the addition of dilute sulphuric acid (page 517), and reported as barium carbonate.

[4] Assuming that the qualitative analysis has shown the absence of lead.

[5] Some prefer to fuse insoluble matter with sodium carbonate. Take up the mass with water, etc., as described below.

"total insoluble" for silica, add sulphuric and hydrofluoric acids. Evaporate to dryness, ignite, and weigh. The loss in weight represents silica.

The alumina, ferric oxide, lime, and magnesia are determined in the filtrate in the usual manner.

Soluble Sulphate.—Boil 1 grm. of the powdered sample with 20 c.c. of concentrated hydrochloric acid; add 200 c.c. of hot water; boil; filter; and wash. Determine the sulphates in the filtrate by the addition of barium chloride (page 618). Multiply the weight of the barium sulphate obtained by 0·5833 to get the corresponding amount of calcium sulphate; and by 0·2402 to get the corresponding amount of CaO. If the amount of CaO so determined be less than that obtained by the oxalic process, above, and if carbonates are present, report the equivalent of the remaining calcium oxide as calcium carbonate; and if carbonates are absent, report the remaining CaO as lime.

Loss on Ignition.—On ignition of a given sample in a platinum crucible, the loss in weight represents water (free, or combined with gypsum or clay); carbon dioxide from the whiting; and organic matter.

Complete Analysis.—A more exact analysis can be made by fusing a couple of grams of the sample with sodium carbonate in a platinum crucible. Digest the fused mass with hot water[1] until the alkaline sulphates and carbonates are all dissolved. Filter the hot solution, and wash the insoluble residue with water. A small excess of hydrochloric acid is added to the solution, which is then evaporated to dryness. The silica is removed by evaporation in the usual manner; and sulphuric acid is determined in the filtrate by the method of page 618. The insoluble residue is dissolved in dilute hydrochloric acid, evaporated to dryness, and the silica filtered off in the usual manner. The two filtrates can then be combined—aluminium and ferric hydroxides are precipitated by the addition of ammonia (page 181); the ammoniacal filtrate is treated for barium, strontium, and lime, etc., by the method of § 271, or § 272, pages 514 and 515.

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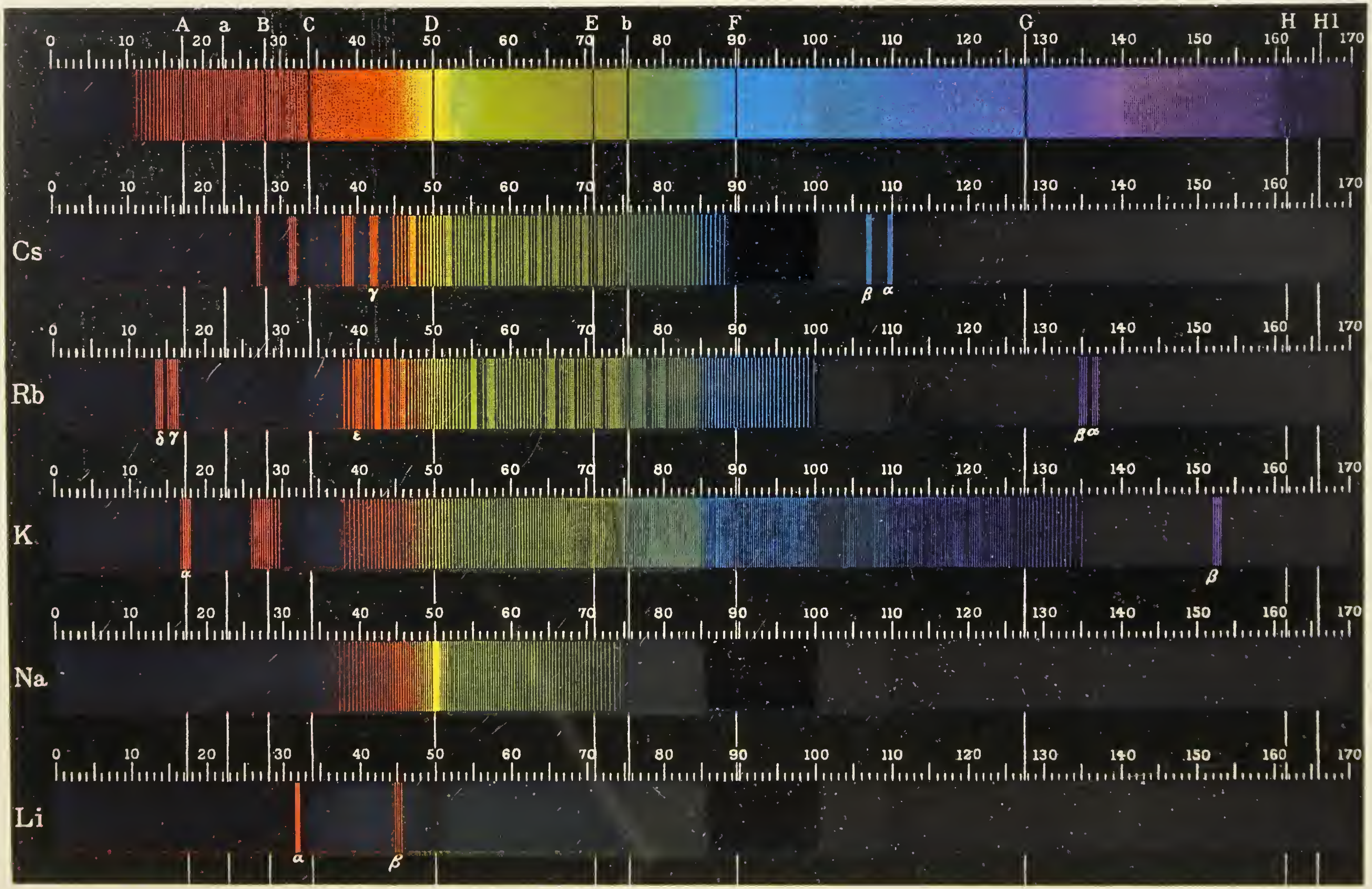
[1] Note, if hydrochloric acid be used for the extraction, insoluble barium sulphate is re-formed. During the fusion: $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$. The latter is soluble in water; the barium carbonate is insoluble. If hydrochloric acid be used, barium carbonate dissolves, and barium sulphate is reprecipitated by the soluble sulphate.

PLATE II.

Chemical Analysis. J. W. Mellor, D.Sc.; London, Charles Griffin & Co., Ltd



Mc Farlane & Erskine, Lith Edinr

CHAPTER XXXVII.

SPECIAL METHODS FOR THE DETERMINATION OF ALKALIES AND THEIR SALTS.

§ 280. The Gravimetric Determination of Lithium—Kahlenberg's Process.

Lithium can be detected in many clays and in most natural silicates by means of the spectroscope, but it is usually present in such small quantities in clays that a quantitative separation is impracticable. Some samples of Cornish stone, however, may have appreciable amounts of lithium.[1] It is generally stated that the lithium will be found in the ordinary course of analysis, mixed with the chlorides of potassium and sodium.[2] As a matter of fact, lithium carbonate is precipitated when a solution of lithium chloride is treated with an alkali carbonate, for 100 c.c. of water, at 10°, dissolve but 1·4 grms.; and 100 c.c. of alcohol, 0·06 grm. of the carbonate.[3] The solubility is, however, much increased in the presence of ammonium salts, so that no precipitate will be obtained if a sufficient excess of these salts be present. Again, when calcium is precipitated as oxalate, lithium is retained so tenaciously that it is exceedingly difficult to wash the lithium from the precipitate. This uncertainty about the location of the lithium salts makes it desirable to proceed a little differently from the method indicated on page 223, when lithium is to be determined.

The Isolation of Lithium Salts.—After treating the calcium oxide, etc., formed during the ignition, in Smith's process (page 222), with water, the aqueous extract is evaporated to dryness in a platinum dish with the occasional addition of concentrated hydrochloric acid. Dry at 110° for about half an hour. Extract the residue with 25 c.c. of 95 per cent. alcohol, and wash with alcohol until the lithium is all removed.[4] Evaporate the washings, etc., to dryness [5] along with a little hydrochloric acid. The residue is now extracted with absolute alcohol until the runnings are free from lithium. Evaporate to dryness as before, and treat the residue with a little dilute hydrochloric acid. Make the solution alkaline with calcium hydroxide,[1] and filter off the precipitated magnesium hydroxide. Precipitate the lime with ammonia and ammonium oxalate in the usual way. Filter and thoroughly wash with water—100 c.c. usually suffice to free the precipitate from lithium. Evaporate the filtrate to dryness, drive off the ammonium salts, and repeat the treatment with dilute acid, ammonia, and ammonium oxalate. After evaporation to dryness as before, the residue containing the lithium chloride, along with traces of potassium and sodium chlorides,[2] is treated by the pyridine or the amyl alcohol process.

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[1] The separation of alumina in the analysis of lithium silicates—according to K. and E. Sponholz (*Zeit. anal. Chem.*, **31**. 521, 1892)—requires four or five precipitations of the alumina with ammonia to get the alumina free from lithium. The basic acetate separation, however, is said to present no particular difficulty.

[2] Along with rubidium and cæsium chlorides. A. A. Anderson, *Min. Eng. World*, **36**. 1055, 1912. For the contamination of potassium chloroplatinate with lithium, see G. Jenzsch, *Pogg. Ann.*, **104**. 102, 1858.

[3] P. A. Flückiger, *Arch. Pharm.* (3), **25**. 542, 1887; C. N. Draper, *Chem. News*, **55**. 169, 1887; G. Geffeken, *Zeit. anorg. Chem.*, **43**. 197, 1905.

[4] Lithium may be detected spectroscopically in the residue when it is present in unweighably small amounts. A small direct-vision spectroscope with a slit will show a crimson lithium band between the yellow sodium line and the red potassium line (Plate II.). The spectra of the alkalies are shown on Plate II. The spectroscopic method will detect $\frac{1}{3,000,000}$ mgrm. of soda; $\frac{1}{1000}$ mgrm. of potash; $\frac{1}{1,000,000}$ mgrm. lithia; $\frac{1}{500}$ mgrm. rubidia (Bunsen).

[5] Recover alcohol in the usual way.

The Solubility of Lithium Chloride in Pyridine.—The separation of lithium from a mixture of alkaline chlorides is based on the fact that the chlorides of sodium and potassium[3] are practically insoluble in solutions of pyridine containing less than 5 per cent. of water, while pyridine with less than 3 per cent. of water has no appreciable solvent action on the chlorides of sodium and potassium. On the other hand, lithium chloride is fairly soluble in anhydrous as well as in aqueous solutions of pyridine.[4] The solubility of lithium chloride in anhydrous and in 97 per cent. pyridine solutions at different temperatures is shown in the diagram, fig. 161. The curious break in the curve with anhydrous pyridine is supposed to be due to the fact that below 28° the solution contains $LiCl . 2C_5H_5N$, and above 28°, $LiCl . C_5H_5N$. The table shows that at 20°, 100 grms. of anhydrous pyridine dissolve 13·39 grms. of lithium chloride, and 100 grms. of the 97 per cent. pyridine (97 vols. anhydrous pyridine, 3 vols. water) at 22° dissolve 14·31 grms. of lithium chloride. Kahlenberg and Krauskoff have based upon these facts a process for the separation of lithium chloride from the other alkaline chlorides.

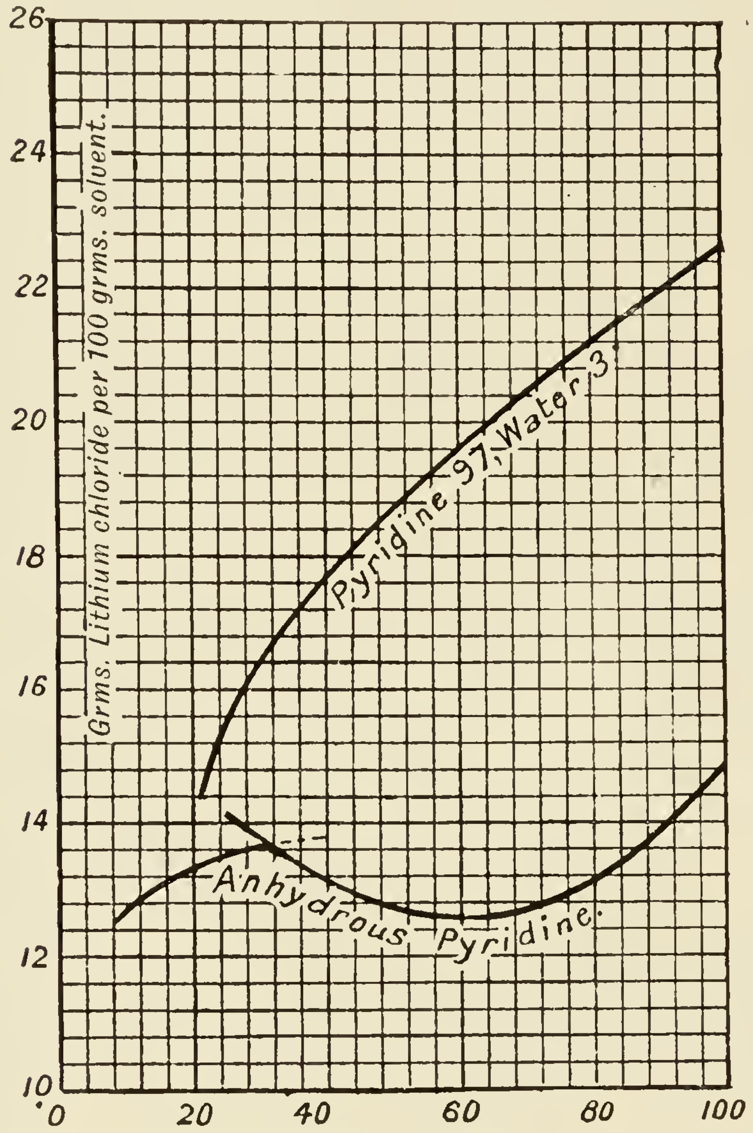

Fig. 161.—Solubility of lithium chloride in pyridine.

1. *First Extraction.*—Evaporate the aqueous solution of the mixed chlorides[5] to dryness. Add a couple of drops of hydrochloric acid.[6] Evaporate the mass again to dryness. Digest the residue

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[1] L. R. Milford, *Journ. Ind. Eng. Chem.*, 4. 595, 1912. Some prefer lime water to baryta water for precipitating magnesium, and thus avoid introducing a foreign substance. Calcium is already present, and calcium oxalate is less soluble and more easily washed than barium oxalate.

[2] If iodides or bromides were present, these salts would be found with the chlorides, since the bromides and iodides are more soluble than chlorides. In that case, an evaporation to dryness with hydrochloric acid and chlorine water, followed by a gentle ignition, will ensure a residue consisting of chlorides only—L. R. Milford (*l.c.*).

[3] Also rubidium and cæsium. According to M. Sérullas (*Ann. Chim. Phys.* (2), 46. 294, 1831), perchloric acid does not precipitate lithium perchlorate from concentrated solutions of lithium chloride.

[4] A. Neumann and J. Schroeder, *Ber.*, 37. 4609, 1904 ; L. Kahlenberg, *Journ. Amer. Chem. Soc.*, 24. 401, 1902 ; L. Kahlenberg and F. C. Krauskoff, *ib.*, 30. 1104, 1908 ; E. Murmann, *Zeit. anal. Chem.*, 50. 171, 273, 1911.

[5] Weighing less than 2 grms.

[6] In order to convert any lithium hydroxide into chloride. The hydroxide is formed by the hydrolysis of the chloride, and the hydroxide is not so soluble in the pyridine.

with about 25 c.c. of boiling anhydrous pyridine[1] for 5 or 10 minutes. Break up any large masses with a stirring-rod with a rounded end. Let the insoluble residue settle. Decant the clear through a small filter paper—6·5 cm. Collect the filtrate in a small Erlenmeyer's flask, and wash the residue with about 5 c.c. of hot pyridine.

2. *Second Extraction.*—Lithium chloride is retained with great tenacity by the insoluble alkali chlorides, and a second extraction is therefore necessary. Dissolve the residue in a small amount of water with a drop of hydrochloric acid. Evaporate the solution to dryness, and repeat the extraction with hot pyridine.[2] Combine the filtrates from the different extractions and washings. Distil off the pyridine by connecting the Erlenmeyer's flask with a small condenser (fig. 162). When the residue in the flask is nearly dry, let the mass cool.

3. *Transformation of Lithium Chloride to Lithium Sulphate.*—Dissolve the mass in water acidulated with sulphuric acid in order to transform the lithium chloride into lithium sulphate. Filter off any organic residue which may be present, and collect the filtrate in a weighed platinum dish. Evaporate to dryness. Drive off the excess of sulphuric acid at a gentle heat. Fuse and weigh. Multiply the weight of the lithium sulphate so obtained by 0·37467 to get the corresponding amount of lithia—Li_2O.

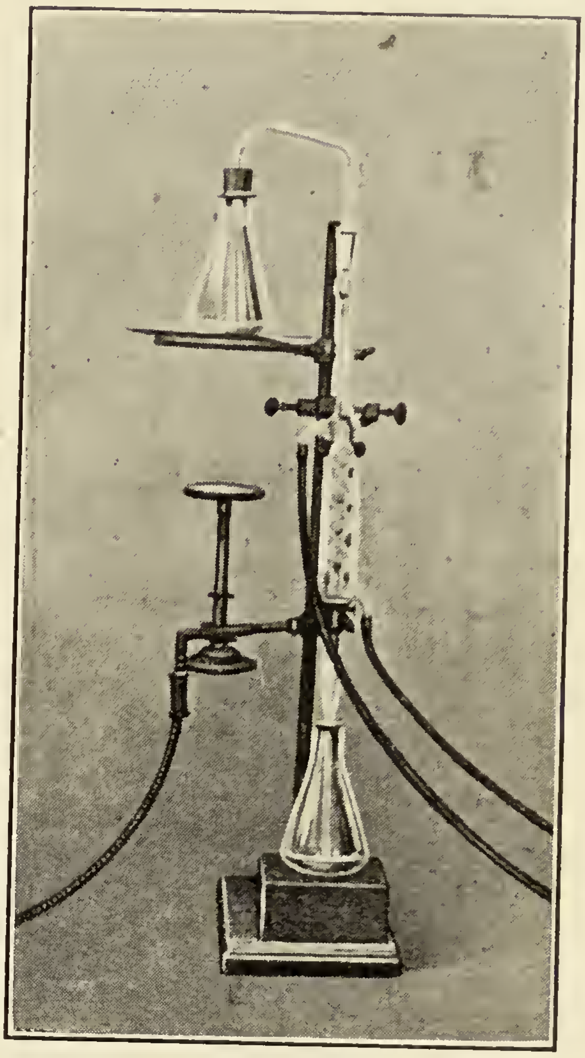

FIG. 162.—The recovery of pyridine.

The most important objection to this process is the unpleasant odour of the pyridine. Hence, the work should be done under a well-ventilated hood. If the odour of the pyridine be considered an insuperable objection, the following is the next best procedure. In illustration of the excellent results which may be obtained by this process, the following experiments with artificial mixtures of lithium chloride with potassium, sodium, and barium chlorides are reported :—

Table LXIII.—Test Analyses for Lithium.

Lithium chloride.		Residue.		Besides lithium chloride, the mixture contained :
Used.	Found.	Used.	Found.	
0·0958	0·0956	0·6007	0·6001	0·2020 KCl ; 0·3082 NaCl ; 0·0905 $BaCl_2$
0·0907	0·0903	0·5867	0·5863	0·1933 KCl ; 0·2913 NaCl ; 0·1021 $BaCl_2$

The Determination of the Potassium and Sodium Chlorides.—If the mixture of alkaline chlorides of L. Smith's process has been under treatment, the residues on the filter papers which have been washed by the 95 per cent. and the absolute alcohol, as well as all the other succeeding residues, are collected together, dissolved in water, and treated as indicated on page 227 *et seq.*, for potassium and sodium.

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[1] Kahlbaum's pyridine may be used for this purpose. The cheaper material (5s. per lb.) should be purified by distillation from fused potash, and the fraction boiling between 114° and 116° be used for the work.

[2] If a relatively large amount of alkaline chloride and a relatively small amount of lithium chloride be present, a third extraction may be advisable.

§ 281. The Gravimetric Determination of Lithium—Gooch's Process.

Gooch's process [1] is based upon the fact that lithium chloride is soluble in amyl alcohol—10 c.c. dissolve 0·66 grm. of lithium chloride—whereas sodium and potassium chlorides are but sparingly soluble in the same menstruum.[2] Gooch has shown that 10 c.c. of the alcohol dissolve 0·0041 grm. of sodium chloride, and 0·0051 grm. of potassium chloride. Hence, if a mixture of lithium, potassium, and sodium chlorides be washed with amyl alcohol, lithium chloride will be removed, while sodium and potassium chlorides remain behind as sparingly soluble residues.

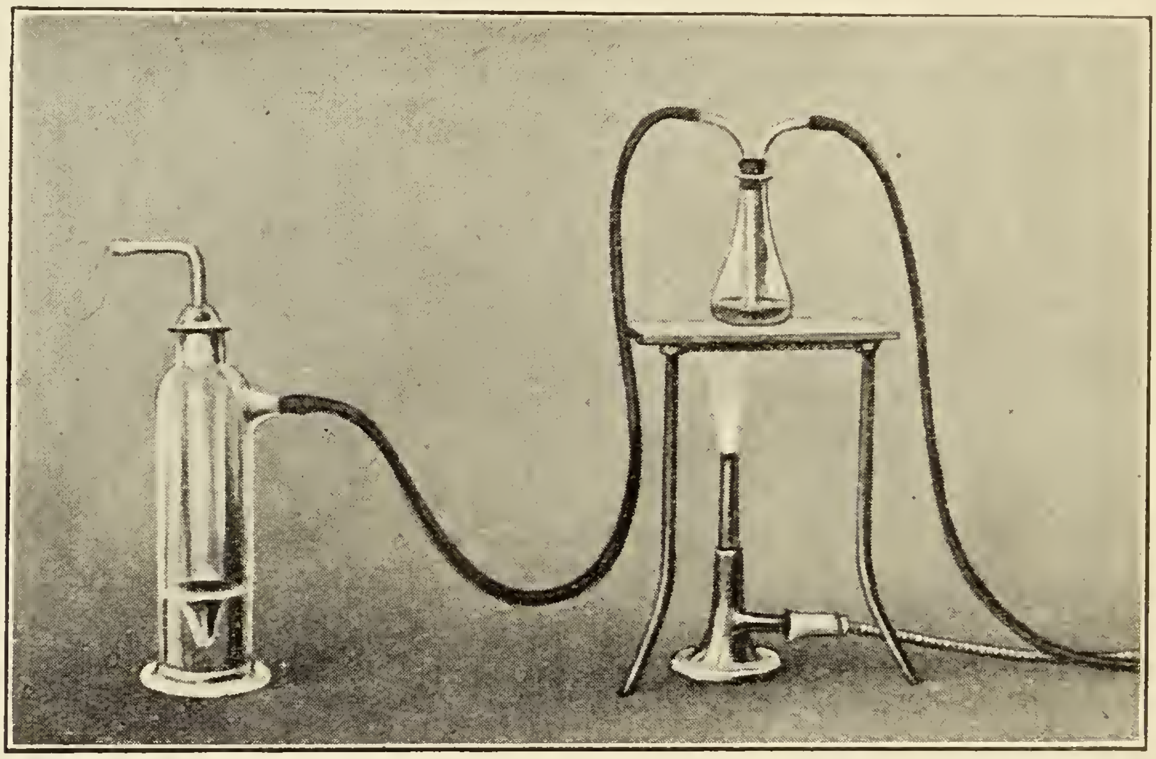

FIG. 163.—Removal of water from amyl alcohol.

The Separation.—The mixed chlorides—say, 0·2 grm.[3] or less—are dissolved in water and filtered into a 50–80 c.c. Erlenmeyer's flask. Evaporate the solution slowly on an asbestos pad over a small flame until the salts show signs of crystallising (1–2 c.c.). Add a couple of drops of water, and a couple of drops of concentrated hydrochloric acid. Treat the concentrated solution of the mixed chlorides so obtained with 10–15 c.c. amyl alcohol (boiling point, 129°–132°) in the Erlenmeyer's flask (fig. 163) fitted with a cork through which passes a capillary tube dipping in the liquid, and also with another tube connected with an aspirator. The flask is heated on an asbestos plate to the boiling point while a current of air is slowly aspirated through the liquid. This prevents any violent bumping of the alcohol, and facilitates the escape of water vapour through the upper layer of amyl alcohol. When the water and about half the amyl alcohol have boiled off, the chlorides of sodium and potassium and a little lithium hydroxide[1] are deposited, while the lithium chloride remains in solution in the alcohol. Let the liquid cool; add two or three drops of concentrated hydrochloric acid in order to transform the lithium hydroxide into chloride. Heat the contents of the flask to the boiling point, and let the whole stand half a minute while aspirating a current of air through the fluid. Filter the hot liquid through a Gooch's crucible packed with asbestos. Wash the precipitate and flask with hot amyl alcohol which has been boiled to remove moisture, until the filtrate shows no trace of lithia. When but small quantities of lithia are in question, redissolve the precipitate in a little water, and repeat the treatment. The volume of the hot alcohol which has been in contact with the undissolved chlorides is noted.[2] Evaporate the united filtrates to dryness in an air bath at a temperature not exceeding 125°.[3] Dissolve the residue in a little water acidulated with sulphuric acid. Filter off the organic residue. Collect the filtrate in a weighed platinum dish, evaporate on a water bath and drive off the excess of sulphuric acid at a gentle heat. Calcine the lithium sulphate in the platinum dish to make sure all the carbon left by the amyl alcohol is burnt. The sulphate is fused one minute. When the dish is partly cooled, cover it with a watch-glass to return any fragments of lithium sulphate which may spit off as the cooling mass contracts. Cool in a desiccator and weigh; again heat the dish up to the fusion point of the sulphate, cool as before, and weigh. The weight is usually constant. Multiply the weight of lithium sulphate so obtained by 0·2726 to get the corresponding amount of Li_2O.

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[1] F. A. Gooch, *Proc. Amer. Acad.*, **22**. 177, 1886; *Amer. Chem. Journ.*, **9**. 33, 1887; *Chem. News*, **55**. 18, 29, 40, 56, 78, 1887; E. Waller, *ib.*, **62**. 173, 181, 1890; *Journ. Amer. Chem. Soc.*, **12**. 214, 1890; W. J. Schieffelin and W. R. Lamar, *ib.*, **24**. 392, 1902; B. Feigenberg, *Eine neue Trennungsmethode des Lithiums von anderen Alkalimetallen*, Berlin, 1905; A. A. Anderson, *Eng. Min. World*, **36**. 1055, 1912; W. W. Skinner and W. D. Collins, *Bull. U.S. Dept. Agric. Chem.*, **153**. 1, 1912.

[2] Rubidium and cæsium chlorides are also practically insoluble in the same solvent—less than 0·009 grm. is dissolved by 10 c.c. of hot amyl alcohol.

[3] If more than this amount of the mixed chlorides be present, concentrate the lithia by digesting the mixed chlorides with 25 c.c. of a mixture of equal volumes of anhydrous alcohol and ether for about an hour in a corked flask. The ether should have been distilled from quicklime; otherwise, the concentration of the lithium is not effected. Some lithium hydroxide remains in the residue. Hydrochloric acid is usually added to retard the hydrolysis of the chloride: $LiCl + H_2O \rightleftharpoons LiOH + HCl$.

Corrections.—A deduction must be made for the potassium and sodium chlorides dissolved by the boiling amyl alcohol in contact with the mixed chlorides. The potassium and sodium chlorides dissolved by the cold amyl alcohol used in the washings are neglected. Subtract 0·00050 grm. for every 10 c.c. from the lithium sulphate of the first filtrate if the lithium is being separated from sodium chloride; and 0·00059 if the lithium is being separated from potassium chloride; and 0·00109 if the lithium is being separated from both sodium and potassium chlorides.

Determination of the Sodium and Potassium Chlorides.—Dissolve the mixed chlorides in the Gooch's crucible in water; evaporate the solution to dryness in a weighed porcelain dish, and weigh. Separate the two chlorides as indicated on page 234. If lithium and sodium are alone being treated, add 0·00041 grm. to the weight of the sodium chloride for every 10 c.c. of amyl alcohol in the filtrate, and 0·00051 grm. to the potassium chloride, if potassium and lithium chlorides are being treated; and 0·00092 grm. if the three chlorides—sodium, potassium, and lithium—are in question.

Errors.—Duplicates with this process agree very well. The chief errors arise from those incidental to Smith's process (page 222), as well as (1) bumping when driving off the amyl alcohol; (2) filtering the amyl alcohol solutions hot; (3) neglect to evaporate the amyl alcohol in the dish at a temperature below the boiling point of amyl alcohol; (4) foaming or spurting when driving off the sulphuric acid from the lithium sulphate; and (5) neglect to protect dish from dust, etc., when the lithium sulphate is cooling. A lithium determination by this process, starting from the dry silicate, occupies about two days.

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[1] Formed by the hydrolysis of the chloride. Lithium hydroxide is but sparingly soluble in amyl alcohol.

[2] Estimate the amount of amyl alcohol in the flask by pouring about the same amount of water into a flask the same size, and measuring the amount of water.

[3] The amyl alcohol rapidly evaporates at this temperature without loss of lithium by spattering.

§ 282. The Evaluation of Potassium and Sodium Salts.

Sodium Nitrate—Chili Saltpetre.

Sodium nitrate or Chili saltpetre generally contains between 95 and 98 per cent. sodium nitrate.[1] The general impurities are potassium nitrate (up to 9 per cent. in extreme cases),[2] sodium chloride, sodium sulphate, sodium iodate,[3] sodium perchlorate,[4] sodium carbonate (rare), magnesium sulphate (rare), and insoluble matter. A common method of evaluating the salt is to determine the percentage moisture, sodium chloride, sodium sulphate, and insoluble matter. These are grouped together as the "refraction," and the remainder is supposed to be sodium nitrate. There are many objections to this process, more particularly if the salt is to be used in the manufacture of nitric acid. Thus potassium nitrate may be present, and this would interfere with the calculated yield of the nitrate.

Determination of Moisture and Insoluble Matter.—For the determination of the moisture, heat 10 grms. of the nitrate in an air bath at 120°–130° until the weight is constant. This takes about two hours. The insoluble matter is determined by digesting 50 grms. of the salt in water and filtering the solution through a tared filter paper, or Gooch's crucible, in the usual manner.

Determination of Calcium, Magnesium, and Iron; Chlorides and Sulphates.—Place 20 grms. of the sample in a filter paper resting in a funnel in the neck of a litre flask. Pour boiling distilled water through the paper. When the solution is cold, make it up to the mark on the neck of the flask with cold distilled water. Pipette 50 c.c. for the determination of chlorides gravimetrically (page 652) or volumetrically (pages 76, 79). Another 50 c.c. are treated with barium chloride, and the barium sulphate determined in the usual manner (page 618). The lime is determined in 200 c.c. by precipitation as calcium oxalate, etc. (page 213). The magnesia is determined in another 200 c.c. by precipitation with ammonium phosphate (page 218). Iron can be determined colorimetrically (page 200).

Determination of Sodium Carbonate.—For the sodium carbonate, evaporate 100 c.c. of the solution to dryness with sulphuric acid, and ignite the residue until the weight is constant. The residue contains sodium, calcium, magnesium, and potassium sulphates Subtract the amount of calcium, magnesium, and potassium sulphates already determined, and the difference represents sodium sulphate. Calculate the equivalent amount of sodium carbonate by multiplying the weight by 0·746.

Determination of Potassium.—The potassium is determined by dissolving half a gram of the salt in an Erlenmeyer's flask in 25 c.c. of dilute hydrochloric acid. Heat the solution to boiling, and add just sufficient barium chloride, drop by drop, to precipitate the sulphates as barium sulphate. Wait after each addition until the liquid has a clear layer, and add the barium chloride until a drop ceases to produce a cloudiness. If too much barium chloride has been added, a drop or two of dilute sulphuric acid will probably make things right by removing the excess of barium chloride. When the solution is cold, treat the clear filtered solution with hydrochloroplatinic acid, etc., as indicated on page 234. See also page 540.

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[1] R. Alberti and W. Hempel, *Zeit. angew. Chem.*, 5. 101, 1892.

[2] G. Lunge, *Chem. Ind.*, 9. 269, 1886; H. Hagen, *Chem. Ztg.*, 15. 1528, 1891; *Zeit. angew. Chem.*, 6. 495, 698, 1893.

[3] H. Beckurts, *Pharm. Centralhalle*, 233, 1886.

[4] H. Beckurts, *Archiv Pharm.*, 224. 333, 1886; H. Fresenius and H. Bayerlein, *Zeit. anal Chem.*, 37. 501, 1898.

Potassium Nitrate, Saltpetre, Nitre.

The moisture is determined as in the case of sodium nitrate. Less than $\frac{1}{4}$ per cent. of moisture is usually present. For the chlorine, dissolve 100 grms. of the salt in water, filter, and wash with hot water. The solution is treated with silver nitrate and the chlorine determined by the turbidity method, or gravimetrically. Less than 0·01 per cent. is usually present. The insoluble matter, sulphates, lime, and magnesia are determined as in the case of sodium nitrate. The sodium is determined as indicated on page 239.

Potassium Carbonate, Pearlash.

The moisture and insoluble matter are determined as just indicated for sodium nitrate. The available alkali is determined by titration as on page 69. The chlorides, sulphates, insoluble matters, silicates, and phosphates are determined in the usual manner. Iron is determined colorimetrically. The total potassium is determined as indicated under sodium nitrate. The results are expressed by calculating the amount of potassium chloride from the silver chloride, and the amount of potassium sulphate from the amount of barium sulphate. Then calculate the amount of potassium carbonate from the difference between the total potash and that corresponding with the potassium chloride and sulphate. Calculate the amount of sodium carbonate from the difference between the available alkali and the potassium carbonate calculated as indicated above. For a further discussion on sodium and potassium carbonates see page 72.

§ 283. The Determination of Potassium Colorimetrically—Cameron and Failyer's Process.

When potassium chloroplatinate is dissolved in water and mixed with an excess of a solution of potassium iodide, the intensity of the red colour so obtained is proportional to the amount of potassium chloroplatinate[1] in the solution. This reaction may therefore be employed quantitatively for the determination of very small quantities of potassium. Ammonium chloroplatinate produces a similar coloration, and therefore all the reagents, and the atmosphere of the laboratory in which the determination is made, must be free from ammonia.

Standard Solution.—Dilute 10 c.c. of standard potassium chloroplatinate solution[2] to about 30 c.c.; add a drop of hydrochloric acid (1 : 1) and $\frac{1}{2}$ c.c. of potassium iodide solution.[3] Let the mixture stand for about an hour to permit the colour to fully develop, and then dilute to 100 c.c. The colour of the test solution is developed at the same time.

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[1] F. K. Cameron and G. H. Failyer, *Journ. Amer. Chem. Soc.*, 25. 1063, 1903; L. A. Hall, *ib.*, 25. 990, 1903; T. T. Morrell, *ib.*, 2. 145, 1880; O. Schreiner and G. H. Failyer, *Bull. U.S. Dept. Agric.* (Soils), 31. 31, 1906.

[2] Standard Potassium Chloroplatinate Solution.—Dissolve 0·0516 grm. of carefully recrystallised potassium chloroplatinate—K_2PtCl_6—in water, and dilute the solution to a litre. Each c.c. of this solution is equivalent to 0·00001 grm. of K_2O.

[3] Potassium Iodide Solution.—Dissolve 25 grms. of potassium iodide in water, and make the solution up to 100 c.c.

Test Solution.—The potassium chloroplatinate is isolated in the usual manner, as indicated on page 234.[1] The salt is collected on the asbestos felt[2] of a Gooch's crucible rather than on filter paper, because of the difficulty in getting filter paper quite free from ammonia. The dried precipitate of potassium chloroplatinate is dissolved in hot water by washing the crucible until about 25 c.c. of filtrate have been obtained. Cool the filtrate; add a drop of hydrochloric acid, and $\frac{1}{2}$ c.c. of potassium iodide solution. After the solution has stood for an hour, dilute to 100 c.c. The comparison is made in the usual manner.[3]

§ 284. The Determination of Potassium—Cobaltinitrite Process.

A solution of sodium cobaltinitrite, $[Co(NO_2)_6]Na_3$—also called Koninck's reagent—precipitates canary-yellow potassium cobaltinitrite when added to a solution of a potassium salt.[4] The corresponding salts of lithium, magnesium, barium, strontium, calcium, iron, aluminium, zinc, etc., are soluble, and hence potassium salts can be readily detected in the presence of these compounds. Cæsium, rubidium, and ammonium[5] salts, like potassium salts, give sparingly soluble cobaltinitrites. The reaction proceeds in presence of chlorides, sulphates, nitrates, phosphates, and acetates. The reaction is quantitative so far as the separation of potassium from sodium is concerned,[6] but the precipitate contains variable quantities of sodium unless the conditions under which the precipitation is made be fairly constant.[7] The precipitate can then be made to approximate closely to dipotassium sodium cobaltinitrite, $[Co(NO_2)_6]K_2Na.H_2O$.

It is maintained by some that the precipitation of potassium as cobaltinitrite is not advisable because of the variable nature of the precipitate just indicated, and because the precipitate is extremely difficult to wash clean. When first formed, the precipitate is granular and settles easily, but it has a tendency to become more or less colloidal as the washing liquids become poor in dissolved salts. The precipitate then filters slowly, and is liable to run through the filtering medium. It has been found possible, however, to cope with these difficulties by evaporating the solution containing the precipitate to a "pasty" mass before filtration and washing. The evaporation also eliminates an error due to the variable character of precipitates formed in solutions of different concentration, and variations which occur when the precipitate is allowed to stand in contact with the mother liquid for different lengths of time. Under these conditions fairly satisfactory results have been obtained.

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[1] Special care must be taken to make sure all the ammonia salts are driven off during the ignition of the mixed chlorides, etc.

[2] The asbestos is washed (page 104), and ignited in a platinum dish to remove all traces of ammonia. Preserve the asbestos in alcohol in a well-stoppered bottle.

[3] If the standard or test solution is the stronger, dilute the stronger solution still more, or take an aliquot portion and dilute it to 100 c.c.

[4] O. L. Erdmann, *Journ. prakt. Chem.* (1), 97. 385, 1866; G. P. Sadtler, *Amer. J. Science* (2), 49. 189, 1870; L. L. de Koninck, *Zeit. anal. Chem.*, 20. 390, 1881; E. Bjilmann, *ib.*, 39. 284, 1900; C. O. Curtmann, *Ber.*, 14. 1951, 2121, 1881; G. Sarr, *Min. Eng. World*, 37. 288, 1912. Potassium can be detected if but 60 parts are present per 1,000,000 parts of solution; if the test be made in the presence of $\frac{1}{100}$N-silver nitrate, the sensitiveness of the test is increased to one part per million (L. L. Burgess and O. Kamm, *Journ. Amer. Chem. Soc.*, 34. 652. 1912).

[5] Ammoniacal fumes should be absent when the work—tests, etc.—is in progress.

[6] F. H. van Leent, *Zeit. anal. Chem.*, 40. 567, 1901; H. Weber, *ib.*, 38. 171, 1899; W. Autenrieth and R. Bernheim, *Zeit. physiol. Chem.*, 37. 29, 1902; W. Autenrieth, *Centr. Min.*, 513, 1908; K. Gilbert, *Die Bestimmung des Kaliums nach quantitativer Abscheidung desselben als Kaliumnatriumkobaltinitrit*, Tübingen, 1898.

[7] R. H. Adie and T. B. Wood, *Journ. Chem. Soc.*, 77. 1076, 1900; M. Cunningham and F. M. Perkin, *ib.*, 95. 1562, 1909; K. A. Hofmann and O. Burger, *Ber.*, 40. 3298, 1907; E. A. Mitscherlich, K. Celichowski, and H. Fischer, *Landw. Ver. Stat.*, 76. 139, 1911; E. A. Mitscherlich and H. Fischer, *ib.*, 78. 75, 1912.

The precipitate need not be ignited and weighed, for it reacts with potassium permanganate as symbolised by the complicated equation : $10[Co(NO_2)_6]K_2Na.H_2O + 22KMnO_4 + 58H_2SO_4 = 21K_2SO_4 + 5Na_2SO_4 + 10CoSO_4 + 22MnSO_4 + 60HNO_3 + 38H_2O$. Hence, the precipitate, and accordingly also potassium, can be determined by a volumetric process.[1] It follows from the equation that $22KMnO_4$ are equivalent to $10K_2O$, and $2KMnO_4$ are equivalent to $\frac{10}{11}K_2O$; or 1 c.c. of $\frac{1}{10}N$-$KMnO_4 = 0{\cdot}0008573$ grm. K_2O.

Preparation of the Sample.—One to five grams of the powdered mineral is decomposed by evaporation to dryness with a mixture of sulphuric and hydrofluoric acids (page 226). The dry mass is extracted with about 50 c.c. of hot water, and boiled with a saturated solution of sodium acetate[2] for 10–15 minutes in a beaker of Jena glass. The precipitated basic acetates of iron, aluminium, titanium, etc., are filtered and washed a few times with hot water. The filtrate is boiled with sodium carbonate. The precipitated magnesium and calcium salts are washed with hot water, and the filtrate evaporated down to about 15 or 20 c.c.

Precipitation of Potassium Cobaltinitrite.—The solution prepared as just described, or by any other convenient process, is mixed in a porcelain basin with, say, 30 c.c.[3] of Koninck's reagent,[4] and 1 c.c. of concentrated acetic acid ;[5] evaporated on a water bath down to a pasty consistence ;[6] and, after cooling, stirred with 25–50 c.c. of water. The precipitate is filtered through an asbestos-packed Gooch's crucible, and washed with sufficient water to remove the excess of the reagent.

Volumetric Determination of the Precipitated Cobaltinitrite.—Transfer the precipitate and felt[7] to a 300-c.c. beaker, and carefully remove any precipitate adhering to the sides of the crucible by means of a rubber-tipped rod and jet of water. An excess of $\frac{1}{10}N$-$KMnO_4$ is added, and the contents of the beaker are boiled until the colour begins to darken. Add 10 c.c. of sulphuric acid (1 : 1);[1] thoroughly stir the mixture; and titrate with $\frac{1}{10}$N-oxalic acid solution until the pink colour of the permanganate just disappears.[2] The difference between the number of c.c. of the $\frac{1}{10}$N-permanganate added, and the number of c.c. of oxalic acid used in the titration, multiplied by 0·0008573 represents the number of grams of K_2O in the given sample. Thus, with a sample of felspar, 0·5 grm. 50 c.c. of $\frac{1}{10}$N-permanganate were added, and 8 c.c. of $\frac{1}{10}$N-oxalic acid were used in the subsequent titration of the undecomposed permanganate. Hence, $(50 - 8) \times 0{\cdot}0008573 = 0{\cdot}036$ grm. of K_2O per 0·5 grm. of sample; or the sample contained the equivalent of 7·2 per cent. of potash (K_2O).[3]

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[1] R. H. Adie and T. B. Wood (*l.c.*) ; W. A. Drushel, *Amer. J. Science* (4), **24**. 433, 1907 ; (4), **26**. 329, 555, 1908 ; *Bull U.S. Agric. Dept.* (*Chem.*), **152**. 42, 1912 ; E. L. Baker, *ib.*, **152**. 28, 1912 ; P. F. Trowbridge, *ib.*, **152**. 184, 1912 ; L. T. Bowser, *ib.*, **152**. 45, 1912 ; *Journ. Ind. Eng. Chem.*, **1**. 791, 1909 ; O. M. Shedd, *ib.*, **1**. 302, 1909 ; **2**. 379, 1910 ; E. A. Mitscherlich, K. Celichowski and H. Fischer, *Landw. Vers. Stat.*, **76**. 139, 1912.

[2] The solution of 5 grms. of the crystalline salt in water should give no yellow precipitate with sodium cobaltinitrite (Koninck's reagent) after standing 24 hours.

[3] A large excess of Koninck's reagent is needed to ensure the coagulation of the precipitate and prevent its running through the asbestos.

[4] KONINCK'S REAGENT.—Dissolve 30 grms. of cobalt nitrate, $Co(NO_3)_2.6H_2O$, in 60 c.c. of water, and add 100 c.c. of a saturated solution (corresponding to about 50 grms.) of sodium nitrite, and 10 c.c. of glacial acetic acid. In a few seconds, a brisk effervescence occurs owing to the escape of nitric oxide, the colour of the solution simultaneously changes to a dark yellowish brown. Since commercial sodium nitrite nearly always contains some potassium salt, some potassium cobaltinitrite usually separates when the mixture has stood a couple of days. Filter the clear solution. The reagent undergoes very little change in three to four weeks if it is kept in dark-coloured glass bottles. The sensitiveness of the reagent which has been kept some time can be tested by adding a few drops to 5 c.c. of distilled water containing one drop of a 10 per cent. solution of potassium chloride. The reagent can be used if it at once produces a yellow precipitate. The reagent which has decomposed and is accordingly useless for the purpose has lost its yellowish-brown colour and become rose-red—W. Autenrieth (*l.c.*). Some prefer to keep the solutions of cobalt nitrate and sodium nitrite in separate bottles and mix the proper proportions for use as required.

[5] The acetic acid prevents subsequent difficulties arising from the sticking of the precipitate to the porcelain dish. If the difficulty still persists, add more acetic acid next time the analysis is made.

[6] If the heat be here too vigorously applied, the viscid liquid is liable to spurt.

[7] It is best to remove the plate to avoid the danger of its becoming coated with manganese hydroxide later on.

Determination of the Potassium in the Cobaltinitrite as Potassium Chloroplatinate or Perchlorate.—According to Autenrieth, the method is most usefully employed as a rapid control process, and for separating the potassium from the other constituents prior to its exact determination as perchlorate or chloroplatinate. In this case, the precipitated cobaltinitrate is collected on a filter paper; the paper is ashed in a platinum crucible, and the precipitate added; the whole is then calcined to dull redness for a few minutes, and the alkali nitrites extracted with hot water. Filter off the cobalt oxide; evaporate to dryness with concentrated hydrochloric acid (sp. gr. 1·124); and determine the potassium as indicated on page 234 or page 237.

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[1] F. H. MacDougall (*Journ. Amer. Chem. Soc.*, **34**. 1684, 1912). "If the sulphuric acid be added to the yellow salt before the permanganate, the amount of permanganate required will be greater than in the regular method . . . owing to the failure of cobaltic cobalt to oxidise nitrites in sulphuric acid solutions under the conditions of the described method."

[2] If manganese hydroxide sticks to the sides of the beaker, add a slight excess of oxalic acid and loosen the precipitate by means of a rubber-tipped rod. Remove the rod and rinse it, since rubber must not be left in contact with potassium permanganate.

[3] After trying the effect of various salts on the results, Bowser (*l.c.*) said: "The greatest danger seems to exist in the case of $MgCl_2$, the iron and the soluble calcium salts. It is unsafe to trust a determination when any of these metals are present. Adie and Wood advised precipitating out all these interfering metals by boiling with sodium carbonate, and this would seem to be the best procedure."

PART V.

SPECIAL METHODS—ACIDS AND NON-METALS.

CHAPTER XXXVIII.

THE DETERMINATION OF CARBON—FREE AND COMBINED.

§ 285. The Direct Determination of Carbon.

A rough idea of the amount of carbon in clays, graphites, etc., can often be obtained by digesting the clay with sulphuric and hydrofluoric acids. The temperature must not be high enough to cause a reaction between the carbon and the sulphuric acid. A slight action can scarcely be avoided. When the acid has done its work, dilute the solution with water; filter through a Munroe's crucible or a tared filter paper; wash;[1] and weigh the dried residue. In view of the many theoretical objections which can be urged against this process, it is surprising how good an approximation can be obtained with a little practice.[2]

Graphitic carbon in the presence of other varieties of organic matter (vegetation, etc.) which cannot be removed mechanically is determined by Mackintosh[3] by the following process, which is based on Schöffel's method for purifying graphite:—Melt some potash in a silver crucible. When the fused mass has stopped spitting, and is in a state of quiet fusion, add the dry and powdered sample under investigation. Keep the temperature of the mass just above the melting point of the potash, and stir occasionally with a silver wire. Raise the temperature a little towards the end of the fusion. When the decomposition is complete, take up the mass with water, filter through a weighed Gooch's crucible, and wash with dilute hydrochloric acid, and finally with a little ammonia in order to dissolve any silver chloride formed by the reaction between the potash and the silver crucible. The graphite remains behind, insoluble; it is scarcely attacked by the treatment. Dry and weigh. Mackintosh says the whole operation occupies about two hours.

Löwe[4] fuses the sample with sodium carbonate, digests the resulting cake with water, and then boils the residue with a solution of sodium hydroxide. The residue is then boiled with hydrochloric acid, washed with water, and dried in a weighed filter, and its weight determined. Silica, etc., can be determined in the aqueous solution from the fused cake. There is always some doubt in both Löwe's and in Mackintosh's processes if the residue is all carbon, and in consequence processes have been devised to burn the carbonaceous residue, and estimate the amount of carbon it contains either by "loss on ignition" or as carbon dioxide.

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[1] Not through asbestos, owing to the attack by the acids. Of course the acids may be neutralised before the filtration.

[2] For filtration with carbon tubes, fig. 53, page 102; and subsequent combustion of the residue, see page 563. O. Johanusen, *Stahl Eisen*, 30. 458, 1910.

[3] J. B. Mackintosh, *Chem. News*, 51. 147, 1885; R. Schöffel, *Jahrb. geol. Reichsanstalt*, 16. 270, 1866.

[4] J. Löwe, *Dingler's Journ.*, 137. 445, 1885; E. Weinschenk, *Zeit. Kryst.*, 28. 300, 1897.

§ 286. The Wet Combustion Process for the Determination of Carbon as Carbon Dioxide.

In the so-called wet combustion process, the finely powdered sample is digested with a mixture of sulphuric acid and chromic acid, or potassium dichromate, or potassium permanganate.[1] The oxygen evolved during the decomposition of the chromates oxidises the carbon to carbon dioxide. The gases are dried, and the carbon dioxide is absorbed as indicated below. These methods appear very simple; so they are. But it is not easy to get good results. It is therefore well to practise the method with a known weight of cane sugar mixed with, say, china clay known to contain no carbon. One gram of cane sugar furnishes the equivalent of 1·544 grms. of carbon dioxide. In this way the beginner may acquire confidence in his work. Details of the procedure are indicated below. The results are usually a little low.

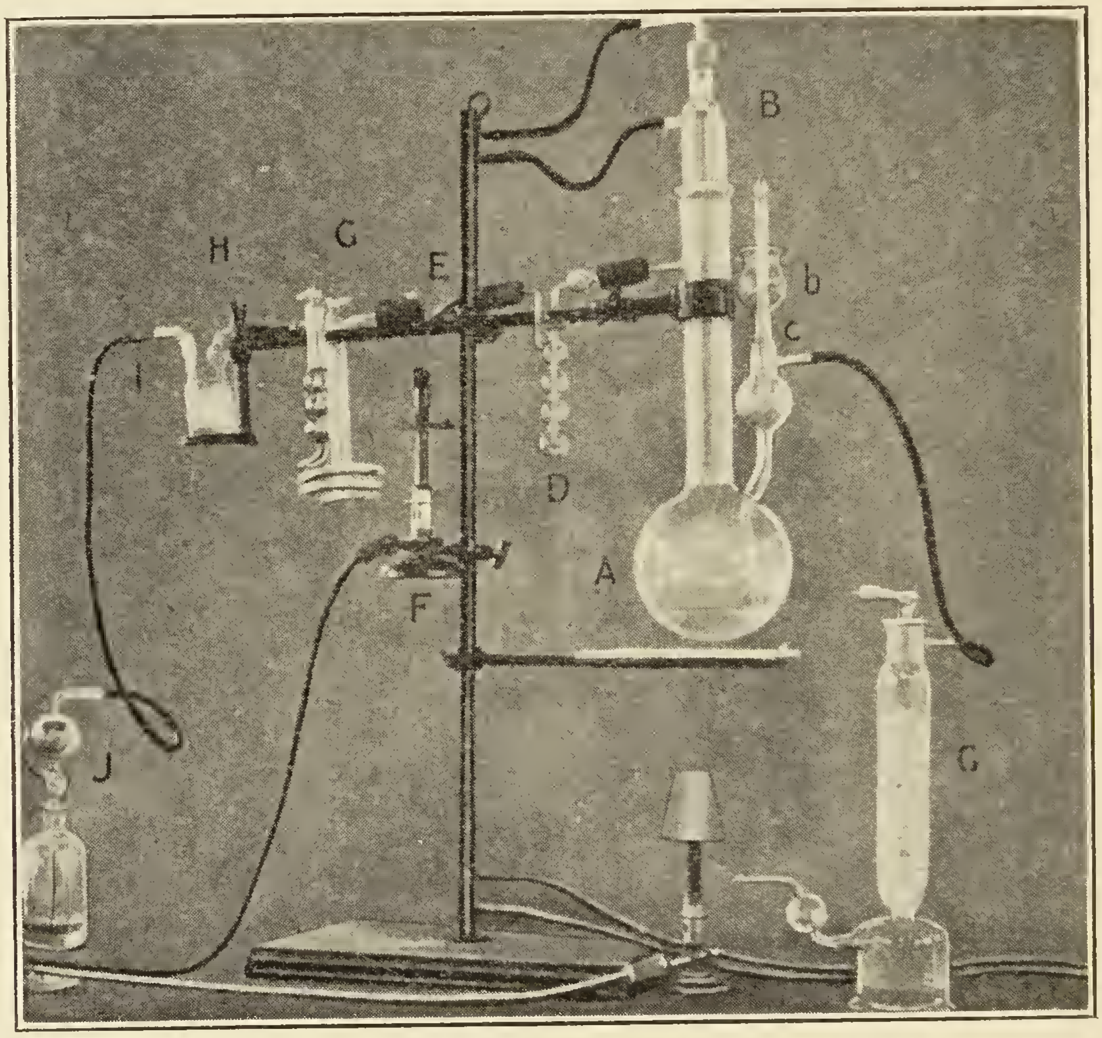

Fig. 164.—Wet combustion of carbon.

1. *The Apparatus.*—A Corleis' flask[2] *A* (fig. 164) contains the powdered clay under investigation. It is closed by a ground-glass condenser *B*. A side tube, reaching nearly to the bottom of the flask, is connected with a

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[1] R. Warington and W. A. Peake, *Journ. Chem. Soc.*, **38**. 6, 17, 1880; C. F. Cross and E. J. Bevan, *ib.*, **53**. 889, 1888; A. H. Elliott, *ib.*, **7**. 182, 1869; R. Phelps, *Zeit. anorg. Chem.*, **16**. 85, 1898; R. Finkener, *Mitt. königl. Ver. Anstalt,* Berlin, 156, 1889; *Zeit. anal. Chem.*, **29**. 666, 1890; R. E. and W. M. Rogers, *Amer. J. Science* (2), **5**. 352, 1848; (2), **6**. 110, 1848; C. Brunner, *Pogg. Ann.*, **95**. 379, 1855; E. Ullgren, *Liebig's Ann.*, **124**. 59, 1862; H. Heidenhain, *Techniker*, **14**. 66, 1893; L. Gmelin, *Oester. Zeit. Berg. Hütt.*, **32**. 708, 1884; H. von Jüptner, *ib.*, **31**. 493, 1883; **34**. 67, 83, 1886; F. A. Cairns, *Chem. News*, **25**. 271, 1872; *Amer. Chem.*, **2**. 140, 1872. Errors—C. F. Cross and E. J. Bevan, *Chem. Ztg.*, **36**. 1226, 1912.

[2] A. Corleis, *Stahl Eisen*, **14**. 381, 624, 1894; A. Kleine, *Chem. Ztg.*, **33**. 376, 1909. Over a score of different forms of flask have been devised for this purpose. A substitute can readily be improvised from an ordinary flask and condenser.

plug stopcock *c*, and a bulb *b* for the reception of the acid to be subsequently brought in contact with the clay under investigation. The side tube is connected with a Fresenius' tower *C* containing an aqueous solution of caustic potash in the lower part, and soda lime in the upper part. The object of the tower *C* is to remove carbon dioxide from any air subsequently aspirated through the system.[1] The purpose of the condenser is to return steam, etc., arising from the flask during an experiment, and so prevent the entry of an excess of moisture into the absorption tubes. The gases travelling past the condenser traverse a White's[2] absorption tube *D* containing an acid solution of silver sulphate[3] to absorb chlorine and vapours of sulphur compounds. The gases then pass through a capillary tube *E* of quartz[4] or platinum, heated to a dull redness by means of the Bunsen's burner *F*. The object of this tube is to oxidise any hydrocarbons, carbon monoxide, etc., which might be imperfectly oxidised by the chromic acid in Corleis' flask.[5] The gases are then dried by passing through a Müller's absorption tube *G*. This tube contains concentrated sulphuric acid. The tube *G* must follow the hot capillary tube *E*, since sulphuric acid is liable to absorb hydrocarbon gases. Any carbon dioxide in the gas is then absorbed by the weighed potash tube[6] *H*, which has a calcium chloride tube *I* attached. Drechsel's wash-bottle,[7] containing potash, protects the weighed potash tube from atmospheric carbon dioxide. The open end of the train *J* is connected later on with an aspirator or suction apparatus in order that a current of air may be drawn through the system when required. The whole may be mounted on a wooden stand or on a Müller's retort stand as shown in the diagram. The condenser is connected with the tubes in the upper part of the stand by means of rubber tubing. The lower tubes of the stand are respectively connected with the water supply and the sink.

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[1] For the difficulties involved in removing the last traces of carbon dioxide from air, see C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, **5**. 52, 1861; *Chem. News*, **3**. 178, 1861; R. E. and W. M. Rogers, *l.c.*; C. Brunner, *Pogg. Ann.*, **24**. 571, 1832; H. Hlasiwetz, *Wiener Akad. Ber.*, **20**. 189, 1856.

[2] J. T. White, *Chem. News*, **58**. 166, 1888. Mitscherlich's tube (A. Mitscherlich, *Zeit. anal. Chem.*, **15**. 389, 1876) or various other forms of absorption tube may be employed, and also other types of flask. Thus, an Erlenmeyer's flask with a three-hole rubber stopper fitted with a separating funnel, a reflux condenser, and a gas leading tube dipping to the bottom of the flask, and connected, when required, with a suitable absorption apparatus for removing carbon dioxide. L. L. de Koninck (*Zeit. anal. Chem.*, **27**. 463, 1888) suggests adding the silver sulphate to the contents of the flask *A*; but although dilute sulphuric acid (2 acid, 1 water, does not appear to act on silver chloride (J. Volhard, *ib.*, **18**. 281, 1879), concentrated sulphuric acid decomposes silver chloride with the evolution of hydrogen chloride (A. Sauer, *ib.*, **12**. 176) 1873; L. Blum, *ib.*, **28**. 450, 1889). Hence, de Koninck's proposal will not do.

[3] Silver Sulphate Solution.—Dissolve 0·624 grm. of silver sulphate in water, add 5 c.c. of normal sulphuric acid, and make the solution up to 100 c.c. The solution is $\frac{1}{25}E$. A tube containing warm lead dioxide is sometimes used to absorb sulphurous gases and haloids. If the lead dioxide be free from lead monoxide, as is the case with "Dennstedt's lead dioxide," there is no danger of the absorption of carbon dioxide. M. Dennstedt and F. Hassler, *Zeit. anal. Chem.*, **42**. 417, 1903; M. Dennstedt, *ib.*, **41**. 525, 1902; F. Kopfer, *ib.*, **17**. 28, 1878; C. M. Warren, *Amer. J. Science* (2), **41**. 40, 1866. Sometimes a heated tube containing silver gauze or wire is used—F. Kopfer, *Zeit. anal. Chem.*, **17**. 28, 1878. The silver is restored by heating in a current of hydrogen—K. Kraut, *ib.*, **2**. 242, 1863. Antimony is sometimes recommended for removing chlorine. A copper spiral was used by C. Glaser, *Liebig's Ann. Suppl.*, **7**. 213, 1870; G. Städler, *Liebig's Ann.*, **69**. 334, 1849. For fluorine, see H. Moissan, *Compt. Rend.*, **107**. 992, 1888; A. Völcker, *Chem. Gaz.*, **7**. 245, 1849.

[4] M. Widemann, *Chem. Ztg.*, **33**. 1186, 1909.

[5] C. F. Mabery, *Journ. Amer. Chem. Soc.*, **20**. 510, 1898; G. Auchy, *ib.*, **20**. 243, 1898; J. Widmar, *Zeit. anal. Chem.*, **29**. 160, 1890; *Chem. News*, **62**. 274, 1890; J. W. Langley, *ib.*, **62**. 218, 1890; *Trans. Amer. Inst. Min. Eng.*, **19**. 614, 1890; A. von Reis, *Stahl Eisen*, **14**. 581, 1893; J. J. Messinger, *Ber.*, **21**. 2910, 1888; A. Müller, *Chem. Zeit.*, **28**. 795, 1904.

[6] I prefer Berl's or Landsiedl's form of potash tube for the reasons indicated on page 551.

[7] E. Drechsel, *Zeit. anal. Chem.*, **15**. 446, 1876.

2. *Charging the Absorption Tubes.*—The Berl's or Landsiedl's potash bulb (figs. 165 and 166) is kept under a desiccator over sulphuric acid or calcium chloride, and it should stand in the balance case about an hour before each weighing. This apparatus is filled with an aqueous solution of caustic potash.[1] Place the potash solution in an evaporating basin; remove the calcium chloride tube *B*; attach a piece of rubber tubing, or a suction tube, to the end which was attached to the calcium chloride tube; dip the opposite end in the potash solution, and suck at the rubber tube until the three bulbs are nearly three-fourths full. Do not suck too vigorously, or potash may be drawn into the mouth. If the tube *A* is wide enough, the potash solution may be introduced by means of a pipette. Clean that part of the apparatus *C* which dipped in the solution by means of filter paper. Now fill the small tube *B* by placing a plug of glass-wool at the end of the tube; then a layer of fragments of granular (not fused) calcium chloride less than half a centimetre in diameter and sifted free from dust; then a similar layer of fragments of soda lime;[2] and finally another plug of glass-wool.[3] The joint *A* is slightly greased. The potash apparatus will absorb about 0·2 grm. of carbon dioxide without re-filling. The contents of the potash apparatus are protected, when not in use, by glass

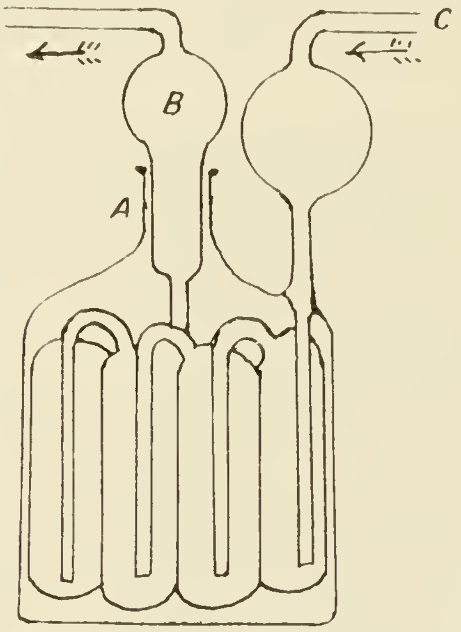

FIG. 165.—Berl's potash bulbs.

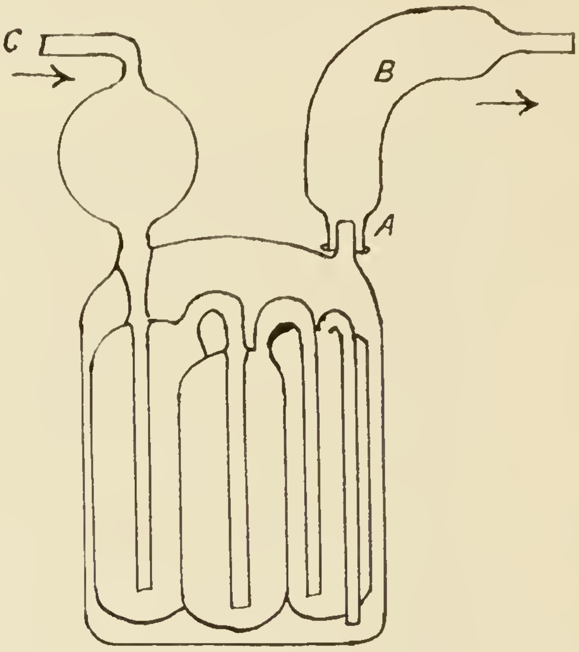

FIG. 166.—Landsiedl's potash bulbs.

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[1] POTASSIUM HYDROXIDE SOLUTION.—A solution of specific gravity 1·4 is made by dissolving 4 parts of the solid in 6 parts of water by weight. Caustic potash is better than caustic soda, since sodium bicarbonate is less soluble than the corresponding potassium salt. The latter is therefore less likely to block the tubes by the crystallisation of the bicarbonate. If the potash should contain any nitrites high results may be obtained, owing to the formation of nitrates—S. C. Jutsum, *Chem. News*, 41. 17, 1880. For the relative efficiency of the different absorption media, see R. Fresenius, *Zeit. anal. Chem.*, 5. 87, 1866; J. Löwe, *ib.*, 9. 220, 1870.

[2] Soda lime loses moisture in air dried by calcium chloride or concentrated sulphuric acid. Hence, some prefer bits of potash in place of the soda lime.

[3] If the soda lime tubes, etc., be packed too tightly, the expansion which occurs as the solid becomes moist may burst the tubes. It is best to interpose layers of glass-wool between the fragments of soda lime. Calcium chloride may contain basic chlorides or free lime, which absorb carbon dioxide and lead to incorrect results if such be placed in tubes *before* the potash apparatus. The faulty calcium chloride will react alkaline to litmus. To render the contamination inert, it is usual to pass a stream of dry carbon dioxide through the calcium chloride for a couple of hours, and remove the carbon dioxide by passing a current of dry air over the calcium chloride for half an hour. C. Winkler (*Zeit. anal. Chem.*, 21. 545, 1882) denies the efficacy of the treatment. He maintains that the lime in the chlorides cannot be completely saturated with carbon dioxide, since the inside of the granules remains caustic after the treatment. Under any circumstances the error mentioned by Winkler is very small, and in the present case this difficulty does not enter into the problem.

caps ground on to the free ends, or short pieces of rubber tubing—2 cm. long—with one end closed by a plug of glass rod about 1·5 cm. long, and rounded at both ends. The apparatus is weighed before and after an experiment with the caps in position. The caps are only removed when the apparatus is to be connected with the train of absorption tubes.

The lower part of the Fresenius' tower *C* is filled to a depth of about 2 cm. with potash lye (sp. gr. 1·4). A plug of glass-wool is placed in the constricted part, and rather coarser fragments of soda lime than those used for the tube *B*, and free from dust, are placed in the upper part. When not in use, the ends of the absorption tubes should be plugged with rubber tubing and glass rod to shut off the air. The stoppers of *C* and *G* render plugs unnecessary.

3. *Charging the Combustion Flask.*—Transfer, say, 1 grm. of the clay,[1] finely powdered and dry (110°), to the Corleis' flask, and add from 5–10 grms. of coarsely granular dry potassium bichromate. If the clay be rich in organic matter less clay may be taken, and the clay is often advantageously mixed with about 10 grms. of dry calcined sand—say Calais sand. Add about 30 c.c. of water, and shake the mixture up, taking care that none of the powder is left stranded above the level of the fluid in the flask. Connect the apparatus as shown in the diagram (fig. 164), and aspirate air throughout the flask and train of absorption tubes for about 10 minutes. Weigh the potash apparatus, and place it in the position shown in fig. 164.

4. *The Oxidation.*—Close the stopcock *c*, light the Bunsen burner *F*. Pour concentrated sulphuric acid into the bulb *b*, and allow the acid to run very slowly into the flask. If no vigorous action occurs, raise the temperature of the flask very slowly.[2] The bubbles of gas should not at any time pass so rapidly that they cannot be easily counted. If the velocity of the reaction be too rapid, the gases may pass through the potash apparatus without being washed free from carbon dioxide, and the calcium chloride tube may not absorb the moisture driven from the potash apparatus. The bulb *b* should be emptied before the flask is warmed, so that the stopcock can be quickly opened in case a sudden pressure be generated in the flask. If the flask should burst and hot concentrated sulphuric acid be sprayed about the operator, the consequences would be serious. With the Corleis' flask the condenser tube or the plug stopcock will be lifted if the pressure becomes very great.[3] A wire gauze between the gas and the Corleis' flask, *A*, is preferable to a sand bath, or to an asbestos or quartz plate, because the temperature of the flask is then under better control. When all the carbon is oxidised, a current of air is aspirated through the system for about 10 minutes.

5. *The Weighings.*—1 grm. of clay was treated as just described. The effect on the potash apparatus was as follows:

Weight of potash bulbs (after)	78·7221 grms.
Weight of potash bulbs (before)	78·5637 grms.
Carbon dioxide absorbed	0·1584 grm.

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[1] The amount of clay to be taken depends on the amount of carbon it contains. The present sample was a black Devonshire ball clay. The potash apparatus should not be made to take more than 0·2 grm. of CO_2.

[2] The bichromate may be dissolved in the sulphuric acid before it is mixed with the clay, as recommended by F. K. Cameron and F. Breazeale (*Journ. Amer. Chem. Soc.*, 26. 29, 1903).

[3] An explosion might occur if boiling sulphuric acid struck the condenser and caused it to crack. At any rate, a stream of cold water from the cracked condenser descending into the boiling sulphuric acid would make things unpleasant. Hence the acid should boil without bumping. Corleis' flasks can now be obtained with the side tube arranged to intercept the drops from the condenser so that they run quietly into the hot acid.

Every 44 grms. of carbon dioxide are equivalent to 12 grms. of carbon; hence, 0·1584 grm. of carbon dioxide is equivalent to 0·0432 grm. of carbon per 1 grm. of clay; or the sample has 4·32 per cent. of carbon. It will be observed that an error of 1 per cent. in weighing, etc., only makes about 0·3 per cent. difference in the determination of the carbon. *The agreement in a number of duplicates does not prove that the results are accurate.* As indicated on page 171, such an agreement shows nothing more than that the method of analysis used will furnish consistent results when conducted in a uniform way. Suppose a constant percentage of carbon escaped decomposition, the duplicates would be consistently too low. In order to make reasonably sure that a result is accurate, it is necessary to show that a similar result is obtained by several different methods. The time involved is, of course, out of question in commercial work; but it is necessary in establishing the accuracy of a method of measurement when it is not possible to operate with mixtures of known composition.[1]

As stated above, there is no special reason why the particular form of apparatus here recommended should be adopted. Once the principle is mastered, there will be no difficulty in devising innumerable modifications. Fresenius, for instance, used nothing but U-tubes and flasks connected by rubber and glass tubing, but he required nine U-tubes and two flasks! By means of more powerful absorbing apparatus, it is now possible to make the apparatus more compact, and to lessen the labour fitting up the apparatus. The time-factor here again presses upon us. A neat and compact apparatus frequently costs more than a "home-made" apparatus, but in routine work the neat and compact apparatus frequently saves time and renders it more difficult to make mistakes. It is generally advisable to let students use "home-made" apparatus in order to acquire skill, ingenuity, and adaptability in an unfavourable environment. Students reared among neat time-saving apparatus may be found wanting when it is necessary to improvise apparatus.

§ 287. The Errors in Analyses involving the Weighing of Absorption Tubes.

It requires some practice to get constant results. In addition to the precautions already mentioned, it may be useful to point out a few more sources of danger.[2]

1. The air leaving the weighed potash bulbs should have the same state of humidity as the air which enters; otherwise, a loss or gain of moisture might ensue. A second weighed absorption tube containing, say, concentrated sulphuric acid can be placed after the potash bulb to prove that no moisture escaped absorption in the absorption tubes during an experiment. A *temoin* (witness) tube in the form of a duplicate potash bulb may follow the one used for the absorption. The object of this vessel is to make sure that all the carbon dioxide passing through the system is absorbed in the first potash bulbs. If the gas from the clay has a tendency to come off in sudden rushes, this second tube is a necessary adjunct to the train (fig. 164).

2. The volume of the weighed tubes is often great enough to render necessary the corrections mentioned on page 25 for differences in the buoyancy of air due to variations of temperature and pressure during an experiment.

3. There is a difficulty in weighing the potash apparatus on account of the difference in the amounts of moisture and gases condensed on the surface of the

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[1] See the cane sugar and china clay experiment, page 546. Dittrich's experiments, page 247. B. Blount and A. J. Levy, *Analyst*, 34. 94, 1909; A. J. Levy, *ib.*, 37. 392, 1912; H. Islam, *Journ. Ind. Eng. Chem.*, 3. 577, 1911.

[2] G. Auchy, *Journ. Amer. Chem. Soc.*, 20. 528, 1898; H. Heidenhain, *ib.*, 18. 1, 1896.

glass before and after a combustion. This is particularly noticeable in damp atmospheres, when the effect may be great enough to stultify an analysis. The glass is exposed to variations in humidity due to the proximity of the absorption apparatus to the sources of heat; latent heat generated by the absorption of carbon dioxide by the potash; handling with moist or greasy fingers; etc. The apparatus is usually wiped[1] with a clean, soft linen or silk cloth in such a way that the glass does not come in contact with the fingers, and allowed to stand in the balance case half an hour before weighing. If the apparatus on re-wiping has the same weight as before, the result is supposed to be right. The simpler types of potash apparatus with a small surface lend themselves more readily to this treatment than the Geissler's and Liebig's potash bulbs once regularly employed in organic analysis. These tubes are too complex to permit a thorough wiping. Regnault and Stas used a tare in the form of an empty potash bulb of similar shape to the one in use, and placed on the "weights" side of the balance during the weighings.[2] These remarks also apply to the determination of moisture by absorption in weighed U-tubes.

Although many different forms of absorption tube are available, our choice is thus limited by the above considerations. Hence, absorption bulbs of the type of Schiff's, Arnold's, Gomberg's, Landsiedl's, Carrasco's, Anderson's, Delisle's, Wetzel's, Classen's, Berl's, Bender and Hobein's, are preferred to the time-honoured bulbs of Liebig, Mitscherlich, Koninck, Schloesing, Geissler, etc.[3] Berl's (fig. 165) and Landsiedl's (fig. 166) bulbs are used in this work.[4] There is a disadvantage in not having the liquid in the different bulbs in communication, because when one bulb is saturated the liquid cannot diffuse into the others. One bulb is thus thrown out of action.[5] For similar reasons to those just considered, I recommend, later on, a calcium chloride tube with but a small surface exposed to the atmosphere (fig. 174, page 561).

When the carbon dioxide is determined by passing the gas through aqueous barium hydroxide, filtering off and weighing the barium carbonate, or by titrating the residual barium hydroxide,[6] the error is eliminated. This is also the case when the volume of the gaseous carbon dioxide is determined.[7]

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[1] Note the possible electrification of glass vessels on rubbing, and its influence on weighing, mentioned on page 8. This error may run as high as 0·020 grm. (E. Bornemann, *Chem. Ztg.*, 32. 125, 220, 1908). The charge disappears slowly by repeatedly touching the apparatus with the fingers. The electrification is more likely to occur in dry, frosty weather.

[2] For instance, the Geissler's bulbs may be weighed on the one pan, and an empty Liebig's apparatus suspended on the opposite arm, so as to leave the pans free for the weights. The magnitude of the error is reduced by the use of this counterpoise.

[3] W. C. Anderson, *Journ. Soc. Chem. Ind.*, 18. 119, 1899; A. Delisle, *Dingler's Journ.*, 279. 167, 1891; A. Dettloff, *Zeit. anal. Chem.*, 46. 717, 1907; C. Mann, *ib.*, 32. 186, 1892; S. Schiff, *ib.*, 28. 679, 1889; A. Landsiedl, *Oester. Chem. Ztg.*, 5. 31, 1903; M. Gomberg, *Journ. Amer. Chem. Soc.*, 18. 941, 1896; C. M. Johnson, *ib.*, 28. 862, 1906; O. Carrasco, *Chem. Ztg.*, 31. 342, 1907; E. Berl, *ib.*, 34. 428, 1910; G. Schöler, *ib.*, 29. 569, 1905; L. Dufty, *Chem. News*, 87. 289, 1903; A. E. Hill, *ib.*, 98. 38, 1908.

[4] Landsiedl's (fig. 166) and Berl's (fig. 165) bulbs are filled by removing *B* (*A* is a slightly greased joint) and introducing the absorbent by means of a pipette, etc. Apply suction at *C*. *B* is plugged with glass-wool, and filled with calcium chloride as indicated page 548. Total weight about 60 grms.

[5] J. Löwe, *Zeit. anal. Chem.*, 7. 224, 1868.

[6] U. Kreusler, *Zeit. anal. Chem.*, 5. 216, 1866; P. Claesson, *Ber.*, 9. 174, 1876; M. Pettenhofer, *Journ. Chem. Soc.*, 10. 292, 1857; *Journ. prakt. Chem.*, 82. 32, 1861; 85. 179, 1862; *Liebig's Ann. Suppl.*, 2. 23, 1863; W. Spring and L Roland, *Mém. Acad. Roy. Belg*, 37. 1, 1887; J. A. Aupperle, *Journ. Amer. Chem. Soc.*, 28. 858, 1906; A. Grégoire, J. Hendrick, E. Carpiaux, and E. Germain, *Ann. Chim. Anal*, 18. 1, 1913.

[7] J. Wiborg, *Berg. Hütt. Ztg.*, 46. 233, 1887; A. A. Blair, *Journ. Amer. Chem. Soc.*, 18. 223, 1896; G. Lunge and L. P. Marchlewski, *Zeit. angew. Chem.*, 4. 229, 412, 1891; E. Donath and W. Ehrenhofer, *Oester. Zeit. Berg. Hütt.*, 45. 285, 1897; W. Hempel, *Verhand. Ver. Beford. Gewerb.*, 640, 1893.

§ 288. The Detection of Carbon Dioxide.

The presence of carbonates is indicated by a sudden effervescence when the substance is treated with dilute acids—sulphuric, hydrochloric, or phosphoric acid. An excess of acid should be used, since some bicarbonates are soluble in water. The experiment is made by placing a little of the substance in a test tube; covering it with dilute sulphuric acid; and warming the contents of the tube. The carbon dioxide which is formed is heavier than air, and may be poured into a second test tube containing a little lime or baryta water.[1] If the second test tube be shaken, a turbidity will be produced if carbonates be present in the sample under investigation.[2] A drop of lime water hanging from the end of a glass rod held just inside the test tube, which contains the substance under investigation, will show a film of calcium carbonate if carbonates be present.

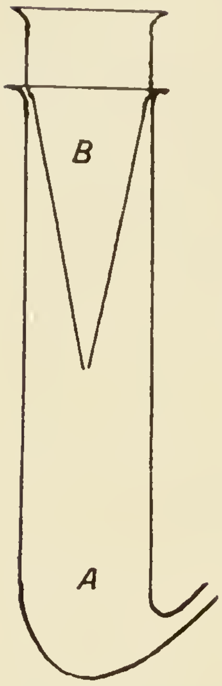

Fig. 167.

The test may also be conducted in the following manner.[3] Draw out the end of a narrow test tube as shown at *A*, fig. 167, and fit a capillary funnel or conical tube as shown at *B*. Put the substance under investigation in the tube *A*, and a drop of baryta water in *B*. Dip the test tube at *A* in hydrochloric acid.[4] The presence of carbonates is shown by a white cloud forming in the baryta water as carbon dioxide passes through.

§ 289. The Rapid Determination of Carbon Dioxide in Carbonates.

As Fresenius remarks, there are few methods of analysis equal in accuracy to a process somewhat similar to that described on page 546; but it requires care and time. There are several short cuts, some of which are quite satisfactory; others, not so accurate, are only justified when time must be abbreviated. There is a remarkable variety [5] of remarkably ingenious and compact instruments in which the acid, the carbonate, and the desiccating agent are placed in separate compartments of one instrument. All are weighed together. The acid is then brought in contact with the carbonate, and when the action is over, the loss in weight represents the carbon dioxide which has left the system. It is not easy to get a degree of accuracy less than about half per cent. with these instruments, except by taking precautions which involve the expenditure of nearly as much time as the gravimetric process next described. If an accuracy of about one per cent. be desired,[1] we can select an instrument from the dealers' catalogues. We naturally reject those which are cumbrous, fragile, difficult to clean, and expensive. Rohrbeck's and Schrötter's are favourite forms.[2]

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[1] The lime water should be kept in contact with calcium carbonate so that the solution is saturated with calcium carbonate, otherwise minute amounts might escape detection owing to the slight solubility of calcium carbonate in lime water—C. L. Berthollet, *Ann. Chim.*, **3.** 68, 1789; H. A. von Vogel, *Schweigger's Journ.*, **33.** 207, 1821; F. H. Storer, *Amer. J. Science* (2), **25.** 42, 1858.

[2] Owing to the fact that air contains carbon dioxide, baryta water will nearly always give a turbidity with a blank test. Hence, the turbidity produced by the carbonate should be more intense than the turbidity produced by the blank test. The two should show a marked difference.

[3] O. Rössler, *Ber.*, **20.** 2629, 1887. In special cases, the test must be conducted in air free from carbon dioxide—see F. P. Treadwell, *Analytical Chemistry*, New York, **1.** 307, 1903. Consult any work on qualitative analysis for confirmation tests.

[4] Dilute sulphuric acid does not always produce effervescence with magnesite, siderite, and dolomite. The "best acid" to use depends upon the nature of the carbonate. Sulphuric acid is suitable for alkaline carbonates; hydrochloric acid for magnesium and calcium carbonates; and nitric acid for lead carbonates—white lead. With nitric and hydrochloric acids there is always a danger of losing a little acid, since some acid may be carried out of the system with the carbon dioxide, especially if the latter comes off rapidly. A. Mayer (*Lands. Ver. Stat.*, **51.** 339) says that if ferrous carbonate be present, dilute acetic acid is best (1 acid, 2 water), because ferrous carbonate is not then attacked, while magnesium and calcium carbonates are attacked. H. Bornträger (*Zeit. anal. Chem.*, **29.** 141, 1890) prefers nitric to hydrochloric acid for small quantities, because hydrogen chloride and chlorine gases are not absorbed by the drying agent—sulphuric acid—whereas nitric and nitrous gases are.

[5] See the dealers' catalogues for a few of the multitudinous forms which have been invented. For a process based on the fusion of sample with sodium paratungstate, see F. A. Gooch and S. B. Kuzirian, *Amer. J. Science* (4), **31.** 497, 1911. The loss in weight of the mixture

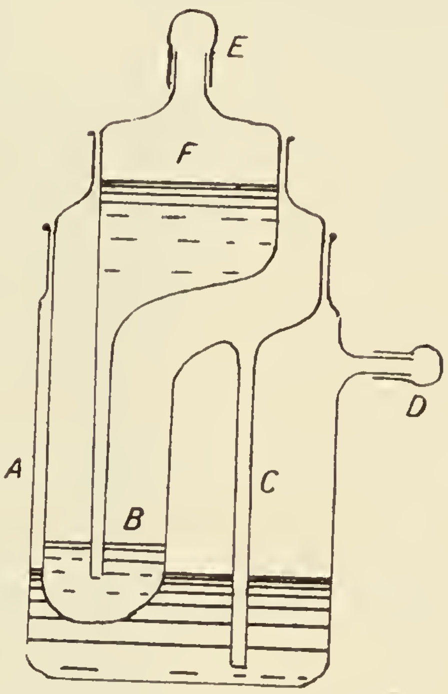

Fig. 168.—CO_2 apparatus.

Fig. 168 represents an apparatus which resembles an ordinary weighing bottle in external appearance.[3] It is easy to clean and fill. Place about a gram[4] of the carbonate under investigation in *B*, and some concentrated sulphuric acid in the outer vessel *A*. The pipette *F* is filled with the required acid (about 5 c.c.) either by suction or by resting the tip *B* on a rubber stopper and introducing the acid by means of a pipette at *E*.[5] The air in the capillary prevents acid running through, and the stopper *E* is inserted before *F* is lifted from the rubber. Everything is then fitted as indicated in the diagram. Wipe the outer tube, and when the vessel has stood in the balance case a short time, it is weighed. The caps *D* and *E* are then removed, acid runs on to the carbonate, the gas bubbles through the concentrated sulphuric acid and escapes *via D*. When all action is over, a slow current of air may be aspirated through the system, by applying suction at *D*, and connecting *E* with a soda lime and calcium chloride tube. Replace the caps, and weigh as before. The loss in weight represents the carbon dioxide which has left the system. The results are improved a little if the weighing bottle be placed in a little warm water while the air is being aspirated through the system.

The following numbers represent the results which might be expected:

Used ($CaCO_3$) . .	0·2153	0·2011	0·2004	0·2006	0·2020	0·2018	grm.
Found ($CaCO_3$) . .	0·2149	0·2010	0·1999	0·2003	0·2017	0·2017	grm.
Error . . .	−0·0004	−0·0001	−0·0005	−0·0003	−0·0003	−0·0001	grm.

§ 290. The Gravimetric Determination of Carbon Dioxide.

With clays containing carbonates it is advisable to determine the carbon dioxide independently of the carbon, and subtract the carbon dioxide from

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before and after fusion represents the carbon dioxide expelled. Processes like this have a limited application. See page 520.

[1] The results are better with substances rich in carbonates.

[2] A. R. von Schrötter's (*Ber. Wien. Acad.*, **63**. 471, 1871), J. Davies' (*Brit. Pat. No.* 533209, 1908), J. L. Kreider's (*Amer. J. Science* (4), **19**. 188, 1905; *Zeit. anorg. Chem.*, **44**. 154, 1905; *Chem. News*, **93**. 62, 1906), C. H. Cribb's (*Analyst*, **21**. 62, 1896), etc., are useful forms. The apparatus—fig. 168—was made for me by Gallenkamps.

[3] The apparatus, slightly modified, can be easily made from regular laboratory apparatus—old pipettes, a weighing bottle, etc.

[4] The amount is determined by the percentage of carbonates in the given sample. We generally have a rough idea. Two or three grams may be used when the substance is poor in carbonates.

[5] The acid should run out slowly in small quantities at a time. This is best arranged by making the capillary tubes *C* and *B* narrow.

the decomposition of the carbonate from the carbon dioxide derived from the combustion of the carbonaceous matters. The carbon dioxide can be accurately determined in an apparatus (fig. 164) modified as indicated in fig. 169.[1] The quartz capillary is to be replaced by a double U-tube *E*, one half filled with pumice saturated with anhydrous copper sulphate,[2] and the other half with calcium chloride. The White's tube *D* contains sulphuric acid. The other tubes, etc., are filled as indicated on pages 348 and 349 in the wet combustion process for carbon.

The amount of clay to be taken for an experiment depends upon the amount of carbonates present. From 5 to 50 grms. of the dried clay are transferred to the flask, and this is made into slip with boiled distilled water free from carbon dioxide. Hydrochloric or sulphuric acid is added slowly by opening the plug cock. When effervescence[3] has ceased and enough acid has been added to decompose all the carbonates, the flask is gently heated for about 15 minutes while a current of air is slowly aspirated through the system.

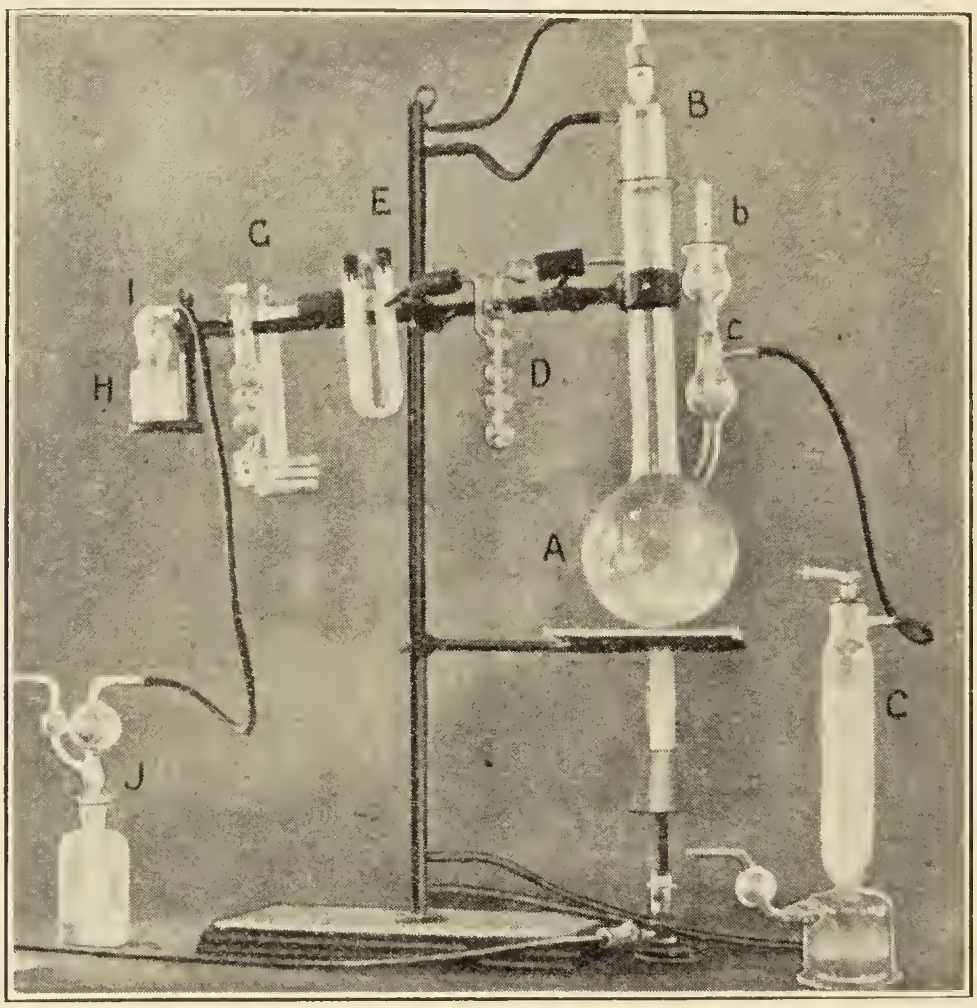

Fig. 169.—Determination of carbon dioxide in carbonates.

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[1] R. Fresenius, *Quantitative Chemical Analysis*, London, 2. 340, 1876 ; *Zeit. anal. Chem.*, **14**. 174, 1875 ; A. Classen, *ib.*, **15**. 288, 1876 ; H. Kolbe, *Liebig's Ann.*, **119**. 130, 1861 ; J. Hessert, *ib.*, **176**. 136, 1875 ; J. Volhard, *ib.*, **176**. 142, 1875 ; H. Rose, *Pogg. Ann.*, **116**. 131, 1862 ; J. Persoz, *Compt. Rend.*, **53**. 239, 1861 ; L. T. Bowser, *Journ. Ind. Eng. Chem.*, **4**. 203, 1912 ; H. W. Brubaker, *ib.*, **4**. 599, 1912 ; E. W. Gaither, *ib.*, **4**. 611, 1912.

[2] F. Stolba, *Dingler's Journ.* **164**. 128, 1862 ; *Zeit. anal. Chem.*, **10**. 76, 1871 ; R. Fresenius *ib.*, **14**. 174, 1875. The pumice is prepared by sifting about 60 grms. of fragments of pumice, about the size of peas, free from dust. The fragments are placed in an evaporating basin with a concentrated solution of copper sulphate (30–35 grms.). Evaporate the solution to dryness with constant stirring. Heat 4 or 5 hours in an air bath at 150–160°, not more, or sulphur dioxide will be formed. The pumice so prepared will remove hydrogen sulphide and hydrogen chloride from the gases.

[3] If the substance froths and foams, it may be necessary to use a comparatively large flask.

In illustration of the weighings, the following numbers may be cited: 2 grms. of clay were treated with dilute hydrochloric acid, and:

Weight of potash bulbs (after)	78·1863 grms.
Potash bulbs (before)	78·1326 grms.
Carbon dioxide	0·0537 grm.

0·0537 grm. of carbon dioxide per 2 grms. of clay represents 2·68 per cent. of carbon dioxide, or 6·09 per cent. of calcium carbonate, since weight of carbon dioxide multiplied by 2·27432 represents the corresponding amount of calcium carbonate, $CaCO_3$; and if the weight of carbon dioxide be multiplied by 1·2748 the corresponding amount of calcium oxide, CaO. Of course, the carbon dioxide may be wholly or in part combined as magnesium carbonate; as dolomite; as ferrous carbonate (siderite); or a basic iron carbonate. If *w* denotes the weight of carbon dioxide, we have

$2{\cdot}2748w =$ Per cent. calcium carbonate, $CaCO_3$
$1{\cdot}9164w =$ Per cent. magnesium carbonate, $MgCO_3$
$2{\cdot}0956w =$ Per cent. dolomite, $MgCO_3 . CaCO_3$
$2{\cdot}6330w =$ Per cent. ferrous carbonate, $FeCO_3$

Success in this determination largely depends upon the speed at which the carbon dioxide is liberated. If the gas comes off too rapidly, some carbon dioxide may pass through the system without giving up its moisture to the desiccating agent.

Concentrated hydrochloric or nitric acid, or dilute sulphuric acid, may be used as indicated on page 552 Morgan[1] recommends orthophosphoric acid (sp. gr. 1·75) for decomposing the carbonates, and then the addition of a moderate excess of chromic acid (3–4 grms.), whereby the carbon is oxidised. Thus carbon dioxide and carbon may be determined separately on the same sample. I have had no experience with this phosphoric acid process.

§ 291. The Volumetric Determination of Carbon Dioxide in Carbonates—Scheibler and Dietrich's Process.

The volume of the carbon dioxide obtained by the action of acids on carbonates can be measured quite accurately. A large number of instruments have been devised and modified for this purpose.[2] Scheibler's instrument is one of the oldest, and, with some modifications, one of the best. Scheibler and Dietrich's instrument, illustrated in fig. 170, is fairly common.

The Apparatus.—In this apparatus, a measuring tube *A* is connected with a levelling tube *B* by means of a piece of thick-walled rubber tubing. *A* is graduated from 0 to 200 c.c.; *B* slides on the upright of the stand. The

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[1] G. T. Morgan, *Journ. Chem. Soc.*, **85**. 1001, 1904.

[2] C. Scheibler, *Anleitung zum Gebrauch des Apparates zur Bestimmung des Kohlensauren Kalkerde in der Knockenkohle*, Berlin, 1862; *Chem. News*, **22**. 75, 1870; R. Warington, *ib.*, **31**. 253, 1875; E. Nicholson, *ib.*, **29**. 245, 1875; H. Fresenius, *Zeit. anal. Chem.*, **19**. 206, 1880; E. Dietrich, *ib.*, **3**. 162, 1864; **4**. 141, 1865; **5**. 49, 1866; D. Sidersky, *ib.*, **25**. 93, 1886; **26**. 336, 1887; E. Jager and G. Krüss, *ib.*, **27**. 721, 1888; R. Baur, *ib.*, **23**. 371, 1884; A. Classen, *ib.*, **15**. 288, 1875; F. Schulze, *ib.*, **2**. 289, 1863; A. Gawalovski, *ib.*, **18**. 244, 560, 1879; G. Burkhardt, *Neue Zeit. Rüb. Ind.*, **16**. 115, 1886; D. Sidersky, *Zeit. Ver. Rüb. Ind.*, **20**. 919, 1885; W. Borchers, *Journ. prakt. Chem.* (2), **17**. 353; G. Lunge, *Chem. Ind.*, **8**. 166, 1885; F. Fuchs, *Chem. Ztg.*, **13**. 873, 1889; R. Finkener, *Zeit. angew. Chem.*, **3**. 273, 1890; W. Thorner, *ib.*, **2**. 641, 1889; E. Cramer, *Tonind. Ztg.*, **18**. 577, 1894.

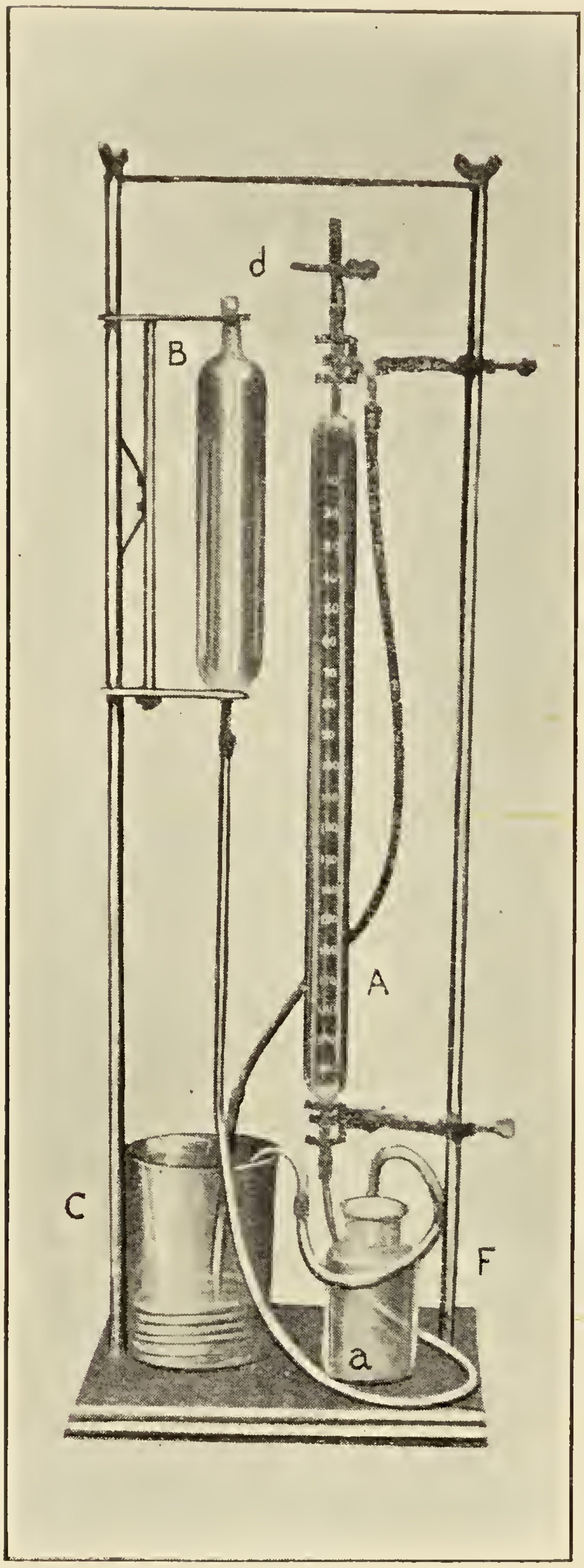

FIG. 170.—Scheibler and Dietrich's apparatus.

upper end of *A* is connected with a three-way cock *d* which connects *A* either with the air, or with a third tube *C* to cool the gases which come from *F*, and flask *F*. *A* is filled with a 1 per cent. solution of boric acid. If all the connections are good, when the liquid in *A* is at zero, it will remain at zero if the levelling tube be depressed for some time, and then raised again.

Adjustment of the Apparatus.—When the instrument is connected up as in the diagram, read the barometer and thermometer. A table is supplied with the instrument. This indicates half the amount of substance to be weighed out for all variations of temperature and pressure between 10° and 25°, and 720 mm. and 770 mm. The right amount of the powdered substance[1] is weighed into the flask *F*, and a small tube containing 5 c.c. of hydrochloric acid (sp. gr. 1·124) is placed in the same flask. The acid tube is reared against the side of the flask, so that the acid does not come in contact with the powder. The flask is closed by means of a rubber stopper. The liquid in *A* is set so that the lower level of the meniscus is at the zero of the scale when the liquid in the levelling tube is at the same level.

Evolution of Gas.—The generating flask is now tilted so that the acid comes in contact with the carbonate. When all action has ceased, and the apparatus has cooled two or three minutes, the level of the liquid in *A* and *B* is adjusted, and the lower level of the meniscus in *A* is read.[2] Add to this a correction for the volume of the carbon dioxide dissolved by the liquid in the generating flask *F*.[3] Half the sum represents the percentage amount of carbon dioxide in the given sample.

§ 292. The Volumetric Determination of Carbon Dioxide in Carbonates—Lunge and Marchlewski's Process.

The apparatus just mentioned gives good results, but it has some weak points. Lunge and Marchlewski[4] have introduced several improvements, but their apparatus, shown in fig. 171, is somewhat expensive (£3, 5s.) Still, it is one of the best instruments for the purpose on the market.

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[1] As indicated in the table, multiplied by 2. The reason for taking the amount of sample different with different temperatures and pressures is to avoid calculating the weight of gas corresponding with the volume measured in *A*.

[2] If after the first action, and the volume of the gas has been read, gas is still slowly evolved from the generating flask, magnesium carbonate is present.

[3] In O. Petterson's method (*Ber.*, 23. 1402, 1890) the carbon dioxide is driven from the generating flask by the simultaneous action of the acid on iron or aluminium wire. Carbon dioxide and hydrogen collect in the measuring flask. The former is determined in an Orsat's apparatus.

[4] G. Lunge and L. Marchlewski, *Zeit. angew. Chem.*, 4. 229, 412, 1891; 6. 395, 1893;

The Apparatus.—In the diagram (fig. 171) *A* is a flask (about 30 or 40 c.c. capacity) closed by a soft rubber stopper. The stopper is fitted with a dropping funnel *a* and a capillary tube bent at right angles, as shown in the diagram. *B* is the gas measuring tube, *D* is the levelling tube, and *C* is a compensating tube whose function is described below. These tubes are connected by means of thick-walled rubber tubing, and mounted as shown in the diagram. *E* is an Orsat's absorption tube containing soda solution or potash.[1] The soda lime tube *F* protects the contents of the Orsat's bulb from atmospheric carbon dioxide. *G* and *H* are three-way stopcocks. The apparatus is used in the following manner :—

Adjustment of the Apparatus.—The decomposition flask *A* is cleaned perfectly free from acid, and an amount of substance which will give not more than 50 c.c. of carbon dioxide is weighed into the flask along with 0·8 grm. of thin aluminium wire.[2] Raise the mercury in *B* until it reaches the stopcock *G*.[3] Connect *A* and *B*, but not *E* and *B*. Depress the mercury in *B* by lowering *D* as far as possible. Turn the stopcock *G* so that when the levelling tube is raised the air in *B* will be driven out of the system. When the mercury reaches *G*, connect *A* with *B*, and repeat the operation three or four times so as to partially evacuate the vessel *A*.

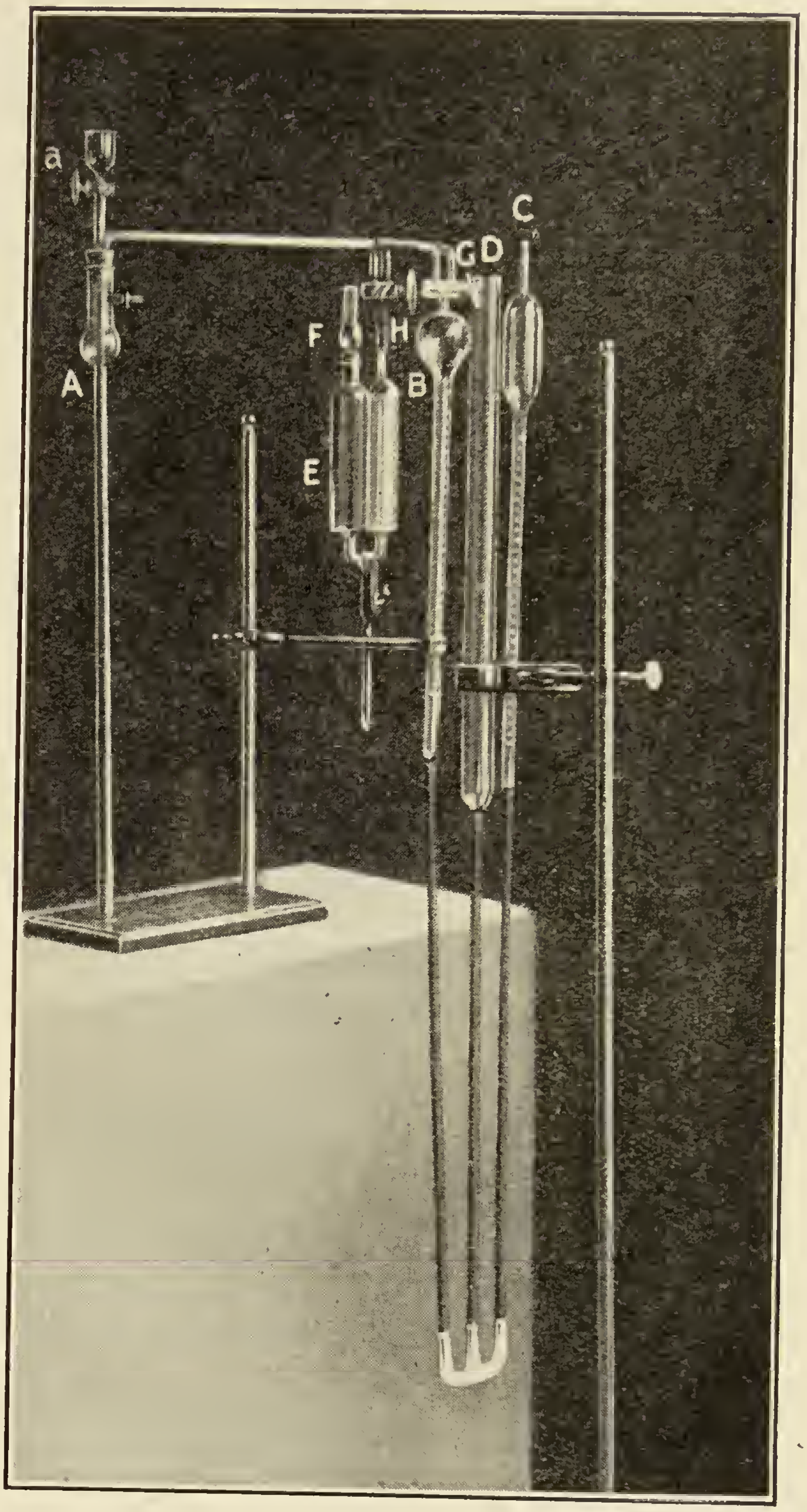

FIG. 171.—Lunge and Marchlewski's apparatus.

Evolution of the Gas.—With the mercury in the levelling tube *C* lower than in *B*, and *C* and *B* in communication, add about 10 c.c. of hydrochloric acid (3 vols. water, 1 vol. acid) *via* the funnel *a*. Close the stopcock of the funnel just before the last drop of acid runs into the flask. Carbon dioxide is evolved at

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W. Thörner, *ib.*, **2.** 644, 1889 ; R. Lorenz, *ib.*, **6.** 395, 411, 1893 ; M. A. von Reis, *Stahl Eisen*, **8.** 257, 1887 ; O. Vogel, *ib.*, **11.** 486, 1890 ; C. Reinhardt, *ib.*, **12.** 648, 1040, 1891 ; G Lunge, *Chem. Ztg.*, **12.** 821.

[1] SODIUM HYDROXIDE SOLUTION.—104 grms. of ordinary caustic soda dissolved in 130 c.c. of water will make about 200 c.c. of a solution approximately 13N. See page 548.

[2] Weigh, say, 10 metres of the thin wire, and calculate the length required to furnish 0·8 grm. Lengths cut this size can be kept in a bottle ready for use.

[3] This requires care, or mercury will be driven where it is not wanted.

once. The mercury in *B* is depressed. Lower the levelling tube *C*, so that, all the time, the mercury in *B* is lower than in *C*. The flask *A* is gently warmed with a spirit lamp for about 2 minutes. Add more acid, and repeat the operation.[1] In this manner nearly all the carbon dioxide is driven from the liquid in *A* by the escaping hydrogen. When all has dissolved, add dilute acid through the funnel to the flask until the flask *A*, as well as the connecting tube, are filled almost as far as the stopcock *G*. Let all stand for about 10 minutes so as to acquire the temperature of the room. Meanwhile the flask *A* and its connecting tube can be removed and cleaned.

Measuring the Volume of the Gas.—Adjust the levels of the mercury in *C* and *D* until the mercury in *C* is at the 100-c.c. mark, and at the same level in *B*. Now read the volume of the gas confined in *B* from the top of the mercury meniscus. Suppose it be 147·5 c.c. The level of the liquid in the Orsat's tube *E* is adjusted by means of the three-way cock *H*, and by blowing through the tube *F* until the soda solution stands at the mark just below the stopcock. Close the stopcock *H*. Let the mercury in the levelling tube stand at a higher level than in *B*. Connect the Orsat's bulb *E* with *B*. Raise *D* gradually until the mercury in *B* is near the stopcock *G*. Then depress *D* until the soda solution stands at its former level. Repeat this operation three times. The soda solution absorbs the carbon dioxide. The motions require care, because it is easy to get the soda solution into the measuring tube *B*, and mercury into the Orsat's tube *E*. A little practice and attention will soon give control of the movements of the fluids. When the level of the soda solution is at its mark below the stopcock *H*, close the cocks *H* and *G*, and adjust *C* and *D* as before. Read the level of the mercury in *B* from the top of the meniscus. Suppose that 108·4 c.c. are indicated. The difference in the two readings represents the volume of carbon dioxide at 0° and 760 mm. pressure given off by the decomposition of the carbonate. We have:

Mercury level before	147·5 c.c.
Mercury level after	108·4 c.c.
Carbon dioxide absorbed	39·1 c.c.

But one cubic centimetre of carbon dioxide at 0° and 760 mm. corresponds with 0·001976 grm. of carbon dioxide, or 0·004497 grm. of calcium carbonate. Hence, 39·1 c.c. of carbon dioxide must correspond with 0·004497 × 39·1 grms. of $CaCO_3$. If 0·1799 grm. of whiting were used in the decomposition flask *A*, it follows that the whiting contained:

$$\frac{0{\cdot}4497 \times 39{\cdot}1}{0{\cdot}1799} = 97{\cdot}75 \text{ per cent. } CaCO_3.$$

Amount of Carbonate required for an Experiment.—It will be observed that we selected a weight 0·1799, which is 2½ times less than 0·4497. Hence, a considerable saving of time is effected by taking, as recommended by Lunge and Marchlewski:

Grams of substance taken.	Nature of the carbonate rock.	1 c.c. of CO_2 represents $CaCO_3$.
0·1799	Very rich in carbonates	2·5 per cent.
0·2248	Marls rich in carbonates	2·0 per cent.
0·4497	Marls poor in carbonates	1·0 per cent.
2·248	Minerals poor in carbonates	0·2 per cent.

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[1] This can be done without admitting air.

If carbon dioxide, not calcium carbonate, be wanted, the factor 0·4497 must be changed to 0·1976, and a corresponding change made in the amount of materials taken for the analysis in order that the number of cubic centimetres absorbed may be a simple multiple or submultiple of the per cent. of carbon dioxide in the substance.

The Compensation Tube.—This is an ingenious device to render the reduction of the gas to the standard temperature and pressure unnecessary. The compensation tube C contains a known volume of air at such a pressure that it has the same volume as it would have at 0° and 760 mm. pressure. If the same temperature and pressure be applied to another gas, it also will take up the same volume it would occupy at 0° and 760 mm. If moist gases be in question, a drop of water is introduced into the compensation tube. From the well-known gas laws, it follows:

$$\text{Volume at } t^\circ \text{ and } p = \text{Volume at } 0^\circ \text{ and } 760 \text{ mm.} \times \frac{(273+t)760}{273(p-f)},$$

where f represents the vapour tension of water at the temperature t, taken from Table LXXXV. To adjust the compensation tube, read the temperature and barometer p. Find the corresponding value of f from table. Calculate the volume which 100 c.c. of gas at 0° and 760 mm. would occupy at t° and p mm. pressure. Adjust the levelling tube by means of the Göckel's stopcock[1] G until the level of the mercury in the compensation tube is at the required gradation. Close the Göckel's stopcock. The tube is then ready for use.

§ 293. The Dry Combustion Process for the Determination of Carbon—Shimer's Process.

One of the best methods for the determination of carbon is to heat the dry clay in a platinum boat in a combustion tube, in a current of oxygen, as is regularly done in the ultimate analysis of organic compounds. The substance may be mixed with copper oxide.[2] The carbon dioxide which is formed, along with the steam, are determined by absorption in suitable vessels. For example, the water is absorbed in a weighed calcium chloride tube; and the carbon dioxide in a weighed potash bulb. The increase in weight of the potash bulb represents the amount of carbon dioxide derived (1) from the carbonates in the clay; and (2) from the combustion of the carbonaceous matters. The former is determined by another operation, and the difference represents that produced by the combustion of the carbon.[3] Chlorine compounds disturb the action. When chlorine is present, the clay may be mixed with lead chromate (free from carbonates, acetates, and nitrates) before it is heated in the current of oxygen.[1] The lead chromate absorbs the chlorine, and some carbon dioxide. The amount of the latter is determined by the method of pages 552 or 553. The remainder of the carbon dioxide will be represented by the increase in weight of the potash apparatus.

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[1] H. Göckel, *Zeit. angew. Chem.*, **13**. 961, 1238, 1900.

[2] G. Gustavson, *Journ. Phys. Chem. Ges.*, St Petersburg, **1**. 416, 1887. J. Persoz (*Zeit. anal. Chem.*, **1**. 83, 1862; *Compt. Rend.*, **53**. 239, 1861) melted the substance with potassium bichromate and collected the carbon dioxide in a weighed potash bulb—J. Hessert, *Liebig's Ann.*, **176**. 136, 1875; J. Volhard, *ib.*, **176**. 136, 1875; R. Fresenius, *Zeit. anal. Chem.*, **14**. 174, 1875. S. S. Sadtler (*Journ. Franklin Inst.*, **144**. 201, 1907) mixed powdered graphite with an accurately weighed quantity of ignited magnesium oxide to prevent the fusion or agglomeration of the ash while the graphite was being ignited in a slow current of oxygen in a crucible. F. Browne (*Chem. News*, **98**. 51, 1908; **100**. 12, 1909) estimates carbon in graphite by ignition of a weighed sample with ferric oxide. The latter is at first reduced, but is afterwards oxidised, so that it remains at the end of the combustion the same as at the commencement. Hence the loss in weight represents the carbon.

[3] Or the carbonates can be removed by digestion in dilute hydrochloric acid, washing, and drying before combustion.

Gooch[2] has devised a very ingenious plan whereby the silicate can be heated in a special "combustion" crucible with or without a flux[3] in a current of oxygen, and the total water, carbon, or carbon dioxide determined in suitable absorption tubes. The Gooch's crucible costs about £20 or £25. This is prohibitive for general use, although it might be worth the outlay when a large number of determinations of "high-temperature moisture" are needed. Several other less expensive forms of "combustion crucible" have been devised. P. W. Shimer,[4] for instance, fits a water-jacketed stopper by means of a rubber gasket into the mouth of a platinum crucible. All is kept cool during the combustion by means of a current of water. This apparatus costs about £8. Sargent, Aupperle, and Eimer have modified the original Shimer's crucible.

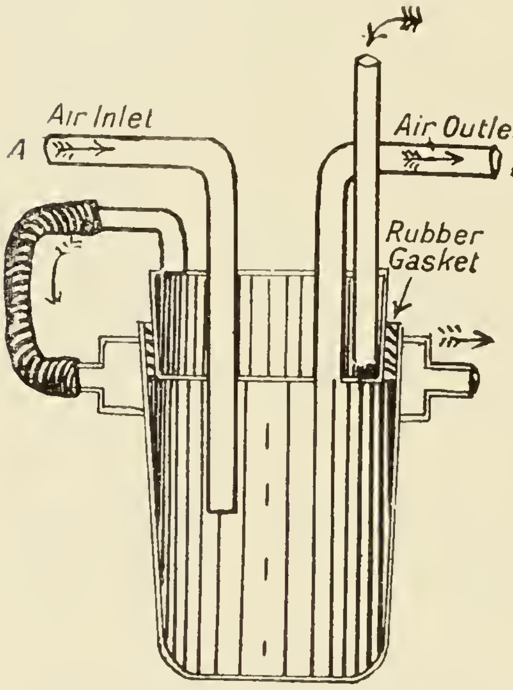

FIG. 172.—Shimer's combustion crucible.

Shimer's Combustion Crucible.—The mouth of Shimer's crucible, shown (somewhat exaggerated) in section in fig. 172, is closed by a small hollow copper cylinder fitted with tubes as shown in the diagram. The stopper is fitted to the mouth of the crucible by means of the rubber gasket which comes between the crucible and the copper cylinder. The crucible is also fitted with a hollow ring. All is arranged so that water can be circulated through the copper head and the hollow ring. In this way, the rubber is kept cool as well as the inlet and outlet tubes. Air or oxygen enters the crucible *via A*, and leaves *via B*.

Adjusting the Apparatus.—The crucible is fitted for a carbon determination somewhat as illustrated in fig. 173. On the extreme left is an arrangement *A* for supplying a current of air or oxygen under a slight pressure. The air or oxygen is purified from moisture and carbon dioxide by passage through a tower of soda lime *B*, and calcium chloride *C*. The latter is connected with the inlet tube of the Shimer's crucible, made either of platinum or nickel. The outlet tube of the crucible is connected with a hard glass tube filled with copper oxide, and kept hot by means of a suitable gas burner. The object of this tube is to oxidise hydrocarbon gases which have escaped oxidation in the crucible. The stream of gases then passes through a weighed calcium chloride tube *F*, whereby moisture is removed, and then through a weighed potash bulb to absorb carbon dioxide. The regular calcium chloride tube packed with the granulated chloride may be employed, when water is to be also

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[1] H. Ritthausen, *Zeit. anal. Chem.*, **22**. 107, 1883; N. N. Ljubavin, *Zurn. russk. Fig. Chim.*, **18**. 480, 1887.

[2] F. A. Gooch, *Amer. Chem. Journ.*, **2**. 247, 1880; *Chem. News*, **42**. 326, 1880; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 78, 1910.

[3] Sodium carbonate freed from moisture and bicarbonates by heating for some hours near its melting point. This is kept in a desiccator. Sodium carbonate is used when water is to be determined; lead chromate if the carbon is also to be determined. See page 520.

[4] P. W. Shimer, *Journ. Amer. Chem. Soc.*, **21**. 557, 1899; **23**. 227, 1901; **25**. 997, 1903: J. V. R. Stehman, *ib.*, **25**. 237, 1903; J. A. Aupperle, *ib.*, **28**. 858, 1906; C. Offerhaus, *Electrochem. Met. Ind.*, **4**. 59, 1906; F. O. Kirchline, *Journ. Ind. Eng. Chem.*, **4**. 683, 1912; and the catalogues of E. H. Sargent & Co., Chicago, and of Eimer & Amend, New York City.
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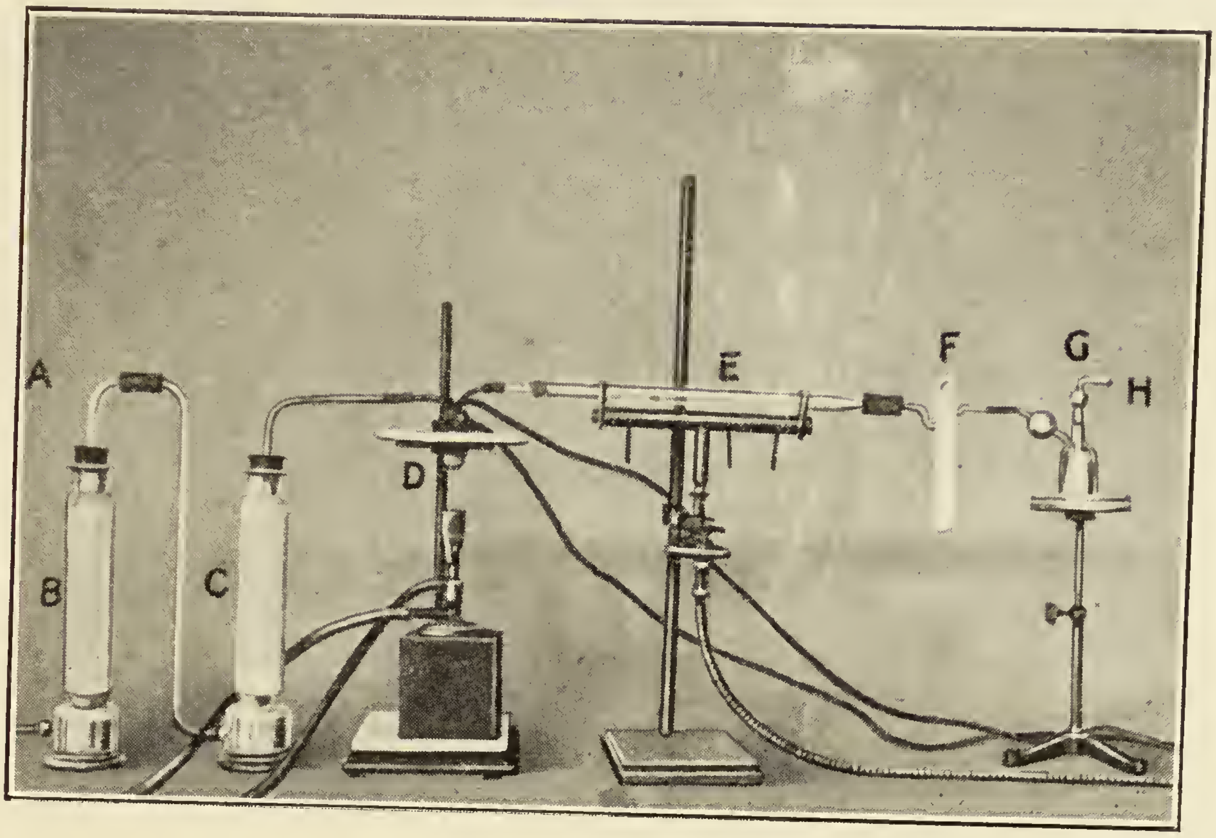

Fig. 173.—Carbon determination by means of the combustion crucible.

determined, or some other form, say, Schütze's or Bender's.[1] The latter is illustrated in some of the diagrams in this work—*e.g.*, fig. 173, and in fig. 174. It is sold packed ready for use, and fulfils the requirements mentioned on page 551 admirably. Finally the gases pass through a guard tube *H* containing calcium chloride to protect the tube *G* from atmospheric moisture. The charging of the different tubes has been described page 548. When all is arranged as indicated in the diagram, the joints must be tested by plugging the exit tube and connecting the gas-holder with the rest of the apparatus. If there is any leakage, the gas will continue bubbling through one or more of the tubes. The gas-holder is then shut off, and the plug taken away very gradually, so that there will not be a violent rush of compressed air from the interior of the system.

When the combustion is completed, the apparatus is allowed to cool while a current of dry air is forced through the system. The calcium chloride and potash bulbs are disconnected and weighed in the ordinary manner.

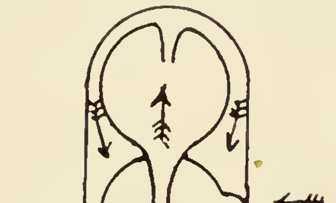

Fig. 174.—Bender's $CaCl_2$ tube.

The Combustion.—If the substance is to be heated without a flux, the crucible is charged by placing a thin layer of ignited asbestos on the bottom of the crucible, the compound under investigation is placed on top, and this is covered by another layer of ignited asbestos. The joint of the lid is shielded from the flame during a combustion by a piece of asbestos board which has a hole cut to fit the crucible. The crucible can also be heated by a blast gas burner. If a flux is used, the crucible should be heated for preference with a blast directed from the side from above downwards, so as to prevent the passage of flux with the escaping carbon dioxide into the exit tubes, and so running a risk of choking the gas tubes. The calcium chloride and potash tubes are weighed as usual.

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[1] R. Schütze, *Chem. Ztg.*, **12.** 722, 1888. A somewhat similar tube is now on the market under the name of "Hill's system"—A. E. Hill, *Proc. Chem. Soc.*, **22.** 87, 1906; G. F. Henning, *Zeit. anal. Chem.*, **40.** 168. 1910. An aluminium foot is sold with the tube, so that the tube can stand upright on the balance pan if it is desired to weigh the tube upright.

Errors.—An objection to all the different forms of combustion crucible has been based on the fact that the flame gases can penetrate the metal (page 372). If the experiment be quickly done, there is no appreciable error; and some recommend using an ordinary platinum crucible with fused sodium carbonate as a kind of outer jacket for the combustion crucible.[1] There is an instinctive feeling that there is a risk of burning the rubber in Shimer's crucible, but experience shows that the fear is groundless, provided the obvious precautions are taken. The lower half of the crucible may be hot enough to burn graphite in air, while the parts in contact with the rubber gasket are so well cooled by the circulating water that the rubber is not affected.[2] Asbestos gaskets may be used when carbon only is to be determined, provided the carbonaceous matters (*e.g.*, dextrine) used as binding agents are removed, and the asbestos is screwed up wet. When determining combined water, rubber is preferable, because wet asbestos is inadmissible, and dry asbestos is inclined to leak.

S. W. Parr[3] determined the carbon by igniting a known weight of the sample in a "bomb" with sodium peroxide (fig. 193, page 623). The resulting product, sodium carbonate, together with any excess of peroxide, is dissolved in as little water as possible, and boiled about 4 minutes to decompose the peroxide and remove all free oxygen. The carbon dioxide in the solution may then be determined volumetrically.

The dry combustion process as conducted in glass tubes will be discussed on pages 563 and 568 in connection with carborundum and graphite.

§ 294. The Analysis of Carborundum.

Grinding the Sample.—Carborundum is so hard that it is impossible to grind it to a fine state of subdivision without a comparatively large amount of contamination (page 120). Again, this substance is so resistant to ordinary chemical reagents that it must be very finely ground if it is to be completely decomposed. Mühlhaeuser[4] has shown that, the coarser the powder, the greater the error in the determination of the carbon, presumably owing to incomplete combustion. He was compelled to stir the powdered material in 2 litres of distilled water, and after settling 1 minute, pour off the liquid with carborundum in suspension. Let this stand 5 minutes and then pour off the liquid. The water contains the so-called 5-min. powder; the 1-min. powder remains as a residue. The stuff which settled after standing 1 minute was reground and again suspended in water. The sample was thus reduced to powders so fine that they remained suspended in water after standing respectively 1 and 5 minutes. These operations are obviously laborious, and occupy a long time—more than a day.

The Determination of Carbon.—The carbon of carborundum and silicon carbides cannot be burned off completely even in a stream of oxygen, although it can be oxidised by fusing the sample with lead chromate (Mühlhaeuser);

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[1] The sodium carbonate is poured out when the combustion is complete and while the flux in the outer crucible is still molten, so as to prevent distorting the crucible by alternate expansion and contraction of the flux.

[2] The rubber should not be used when it is hard and brittle, or it will not make a good joint.

[3] S. W. Parr, *Journ. Amer. Chem. Soc.*, **26**. 294, 1904; **22**. 646, 1900; **25**. 184, 1905; P. Mahler and E. Joutal, *Compt. Rend.*, **153**. 549, 1911; **154**. 1702, 1912.

[4] O. Mühlhaeuser, *Zeit. anal. Chem.*, **32**. 564, 1893.

red lead (Johnson); lead monoxide (Schwarz); lead peroxide; bismuth tetroxide, Bi_2O_4; or a mixture of potassium carbonate and nitrate (Moissan).[1]

A thoroughly clean and dry combustion tube of hard glass[2] is fitted with one-hole rubber stoppers. A plug of ignited fibrous asbestos about 1 cm. long, and about 5 cm. from the end, is placed in the tube. Fill 15 cm. of the tube with coarsely granular lead chromate.[3] Then mix 0·2 to 0·3 grm. of the powder under investigation with 20 times its weight of powdered lead chromate, and transfer the mixture to the combustion tube. Then fill up the tube to within 10 cm. from the end with more granular lead chromate. Insert another centimetre plug of ignited asbestos. Connect this end of the tube (fig. 175) with an efficient drying apparatus, *B*, fig. 176. Gently tap the tube so that a channel is left above the powder for the passage of gas. Connect the other end of the tube[4] with a calcium chloride tube, *C*, and a set of potash bulbs, *D*. Test the joints by closing the left side of the drying apparatus. An aspirator is connected on the right side of the system. If, in a few minutes, no air bubbles through the wash-bottles, the apparatus is fit for work. Aspirate a current of air slowly through the washing apparatus *B* and the rest of the system for about an hour. Then connect the drying apparatus[5] on the left of diagram (fig. 175) with a gas-holder *A* containing oxygen. Disconnect the aspirator. Weigh the calcium chloride tube and the potash bulbs. Adjust the stopcock of the gas-holder (capacity, say, 4 litres) so that oxygen bubbles through the apparatus at the rate of 2 or 3 bubbles per second. Light the burners on the extreme right to within 10 cm. of the powdered substance, with the flame high enough to just warm the tube. Gradually light the burners towards the left, so that the temperature of the powder is gradually raised. Increase the speed of the

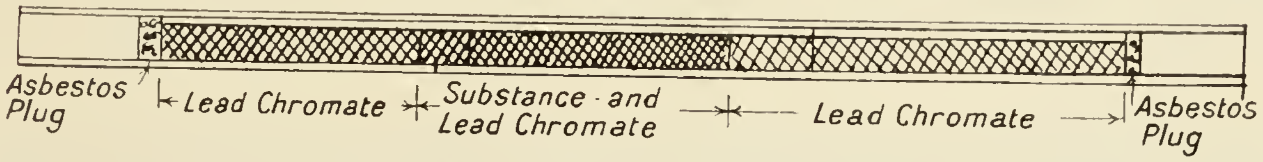

Fig. 175.—Diagrammatic sketch of combustion tube.

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[1] O. Mühlhaeuser, *Zeit. anal. Chem.*, 32. 564, 1893; H. Wdowiszewski, *Chem. Ztg.*, 34. 1209, 1910; R. Amberg, *ib.*, 34. 904, 1910; C. M. Johnson, *Journ. Amer. Chem. Soc.*, 28. 862, 1906. The powder may explode with lead chromate and potassium bichromate (W. Mayer's mixture, *Liebig's Ann.*, 95. 204, 1880). H. Schwarz, *Dingler's Journ.*, 169. 284, 1863. A. Goetzl (*Chem. Ztg.*, 26. 967, 1902) heats the sample with an excess of lead oxide out of contact with air. If more metallic lead is obtained than is required by theory, the sample contains an excess of graphite; and if less, an excess of sandy matters. The carbon dioxide formed during the combustion can be absorbed and weighed. G. Chesneau (*Ann. Chim. Anal.*, 13. 85, 1908) heats a gram of the finely powdered sample to redness for 2 hours in a muffle—loss in weight represents free carbon. Digest the residue with 20 c.c. of hydrofluoric acid and 1 c.c. of sulphuric acid on a sand bath. Boil with hydrochloric acid, add hot water, wash by decantation, and collect on a filter. Ignite and weigh the residue as carborundum. A. L. Queneau, *Met. Chem. Eng.*, 9. 441, 1911; H. de Nolly, *Rev. Met.*, 8. 391, 1911; H. Moissan, *Compt. Rend.*, 117. 423, 1893.

[2] Inside diameter 13 mm., walls 1–1½ mm. thick, length depends upon the furnace. The tube should project 5–8 cm. from each end of the furnace. The sharp ends of the tube should be rounded in the flame. The tube should be dried by passing a current of clean dry air through the warm tube. In drying tubes by a blast of air, dust must be removed from the air by a suitable filter—A. B. Dixon, *Chem. News*, 59. 308, 1889.

[3] Dried at 109° and cooled in a desiccator just before use.

[4] An asbestos plate is generally fitted over the end of the combustion tube near the calcium chloride tube.

[5] An apparatus of this type is usually kept in laboratories for drying air, etc., required in carbon determinations. The one shown in the diagram is Täuber's design—E. Sauer (*Zeit. anal. Chem.*, 31. 195, 1892). Only one side is in use at a time. The wash-bottles contain potash lye (4 grms. solid potash, 6 grms. water). The side of the U-tube next to the wash-bottles is filled with soda lime mixed with glass-wool (page 548); the other limb of the U-tube is filled with calcium chloride (granulated and free from dust). F. Bolm, *Chem. Ztg.*, 27. 1037, 1903.

oxygen towards the end of the analysis. The speed should never be greater than will permit the bubbles to be easily counted.[1] When the tube is dull red, and all the moisture has been driven into the calcium chloride tube,[2] lower the height of the flame, and in about 5 minutes extinguish the flame.[3] Replace the current of oxygen by a current of air. In about 20 minutes, remove the potash bulbs and the calcium chloride tube, and in about half an hour weigh them. The increase in weight of the potash bulbs represents the carbon dioxide formed by the combustion of the free and combined carbon in the given sample. Multiply the result by 0·273 to get the amount of carbon equivalent to the carbon dioxide absorbed in the potash bulbs. The increase in weight of the calcium chloride tube represents the combined hydrogen and the water in the given sample. The carbon is usually a little low, and the water a little high.[4]

The Determination of the Silica.—The silica is determined by fusing the powder[5] with sodium carbonate as for clays; or by fusing with sodium peroxide.[6]

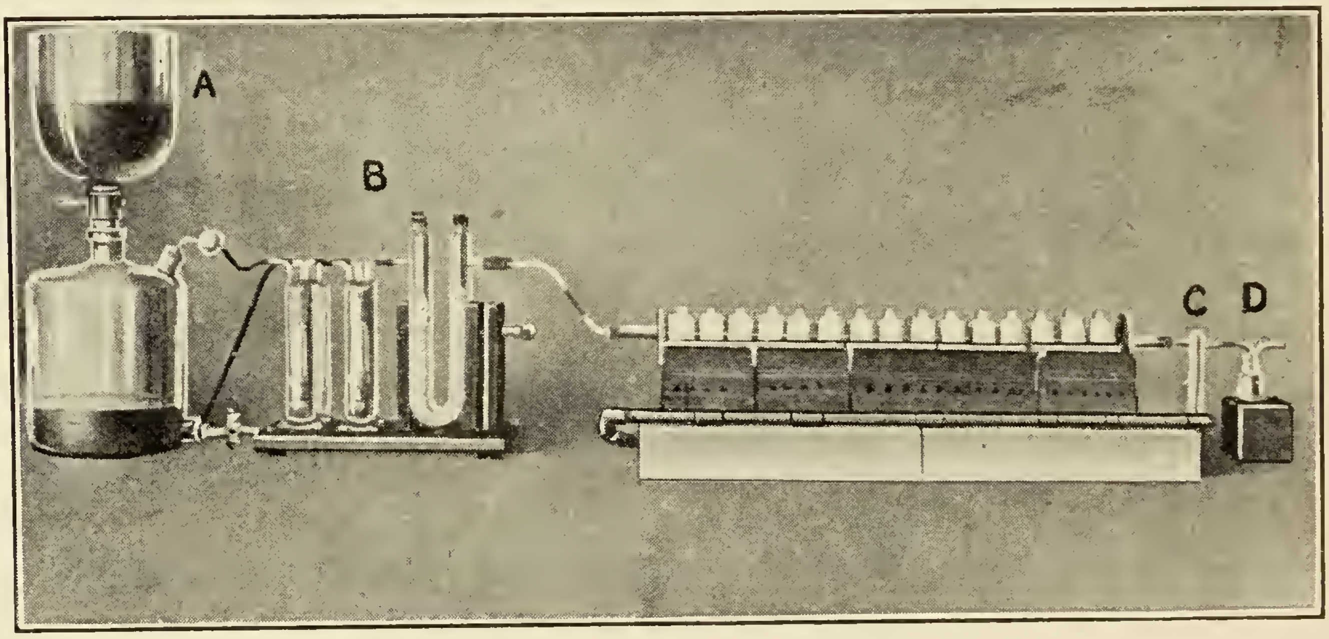

FIG. 176.—Dry combustion process for carbon.

The time required for the fusion is much longer than for clays, and it is necessary to watch for any undecomposed powder in the residue remaining after the fused mass has been taken up with water and acid. If any be present, a re-fusion of the undecomposed residue is necessary.[7] The liquid obtained from the sodium carbonate fusion is treated exactly as described for clays (page 167).

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[1] About 4 bubbles per second—G. Auchy, *Journ. Amer. Chem. Soc.*, **24**. 1206, 1902.

[2] Assisted, if necessary, by the cautious application of a small flame at the end of the combustion tube near the calcium chloride tube. Be careful not to heat the stopper.

[3] Some very neat and convenient electric furnaces have been devised for use where an electric current is available. Hoskins Manufacturing Co., Detroit.

[4] R. de Roode, *Amer. Chem. Journ.*, **12**. 226, 1890.

[5] Mühlhaeuser (*l.c.*) separates the 5-min. powder into 1-min. and 5-min. powders. The latter is used for the carbon determination, the former for the silica, alumina, etc., determination.

[6] S. W. Parr (*Journ. Amer. Chem. Soc.*, **30**. 764, 1908) recommends the use of a fusion mixture: 10 grms. sodium peroxide; 1 or 2 grms. of boro-magnesium mixture; 0·3 to 0·5 grm. of the carbon compound under investigation. The boro-magnesium mixture is made from: boric acid in fine powder, 5 parts; potassium nitrate powdered, 4 parts; magnesium powdered, 1 part.

[7] The reaction is sometimes represented by the symbols: $SiC + Na_2CO_3 \rightarrow Na_2SiO_3 + 2C$. Hence, if a dark-coloured residue remains, it does not necessarily mean undecomposed powder. It may be unburnt carbon. The suspended undecomposed matter is filtered off, washed, calcined in a platinum crucible, and re-fused with sodium carbonate. The cooled mass is taken up with water and acid and mixed with the main portion.

Very few investigations have been made on the analysis of carborundum and silicon carbides. We sometimes have to deal with silicon carbide present in old graphite crucibles,[1] and with carborundum admixed with clay in compounding certain bodies. In that case, Mühlhaeuser's method of grinding must be rejected. The 1-min. powder has a different composition from the 5-min. powder. The grinding need not be so protracted if the alkalies have not to be determined.[2] The substance may then be first broken in a hard steel mortar, and finished with an agate mortar and pestle. 0·5 grm. may be calcined for loss on ignition[3] in a platinum crucible. A crucible with 1 grm. of powdered carborundum weighed 27·9834 grms. After 20 minutes' calcination over a Bunsen's burner, the whole weighed 27·7413; after another 12 minutes' calcination, 27·7390 grms.; after 25 minutes' further calcination on the blast, 27·7398; after 20 minutes' more blasting the weight was 27·7415. No marked change in weight occurred with a more prolonged blasting. The increase is probably due to oxidation of ferrous oxide (page 157). The calcination for loss on ignition is to be conducted over a Bunsen's burner until no further loss in weight occurs. Carborundum gave a loss of 0·88 per cent., followed by a slight gain in weight on further calcination. A known weight is mixed with 5 to 6 grms. of red lead,[4] or lead carbonate, and a gram of sodium nitrite. The mixture is fused over a small Méker's burner to ensure oxidising conditions. When the melt is clear, cool the hot crucible with its lid in position by plunging the hot crucible in cold distilled water. The cake is usually easy to loosen with dilute nitric acid (not hydrochloric acid). Transfer the mass to an evaporating basin and evaporate with concentrated nitric acid to dryness. The fragments gradually soften, and they can be rubbed with an agate pestle from time to time. The dry mass is treated for silica, as described for clays, but nitric acid is used in place of hydrochloric acid. The filtrate is treated in the cold with hydrochloric acid in order to precipitate most of the lead as chloride. Filter off the lead chloride, and wash with hydrochloric acid (1 : 1). Evaporate the filtrate to dryness and take up the residue with hydrochloric acid (1 : 4). Saturate the solution with hydrogen sulphide. Filter off the lead sulphide. Boil the filtrate to expel the hydrogen sulphide. The alumina may then be determined in the solution in the usual manner (page 182).

The Estimation of Silicon Carbide—SiC.—There is a difficulty in calculating the amount of silicon carbide from the analytical data. For instance, suppose that the analysis furnishes:

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[1] Formed in the body of the crucible itself while in use.

[2] Which is not usually the case. Wdowiszewski (*l.c.*) puts for his final analysis: "$K_2O + Na_2O +$ analytical errors 1 per cent."

[3] Note the difficulty with "loss on ignition" owing to the fact that silicon carbides do not burn even in a current of oxygen. The object of the ignition is to burn off as much of the carbon as possible in order to prevent the reduction of the lead oxide to metallic lead, which would ruin the platinum crucible. If alkalies are to be determined, the sodium nitrite must, of course, be omitted.

[4] The red lead must be specially purified, or a blank analysis made so as to be able to correct the final product for silica, alumina, etc. If the red lead contains particles of metallic lead, it will spoil the platinum crucible. The red lead is conveniently made by treating an aqueous solution of pure commercial lead nitrate with a saturated solution of oxalic acid containing 3 per cent. of nitric acid. The precipitate is separated, washed, dried, and ignited at a dull red heat for some hours. Lead carbonate is made by precipitating a solution of lead acetate with the calculated amount of ammonium carbonate, etc. If the sample under investigation contains organic matter, the carbon should be destroyed by gentle ignition. A. F. Crosse (*Journ. Chem. Met. Soc. S. Africa*, 2. 182, 1897; *Chem. News*, 76. 253, 1897), in "assaying graphite crucibles," mixes graphite crucibles with enough manganese dioxide to burn all the graphite.

	Per cent.
Silica	48·34
Carbon	50·12
Alumina and ferric oxide	16·07
Magnesia	0·53
Lime	1·02
Potash	0·21
Soda	0·09
Total	116·38

This result assumes that all the silicon is present as silica. Some is present as silicon carbide, presumably SiC. It is assumed that if the amount of SiC, free silica and combined silicon, and free and combined carbon had been determined, the total would have been 100 instead of 116·38. Part of the oxygen which we have supposed to be combined with the silica was not present in the given sample. Since 32 parts of oxygen correspond with 60 parts of silica, 16·38 parts of oxygen correspond with 30·71 parts of silica.[1] Hence, 48·34 less 30·71 = 17·63 per cent. of free silica. Again, 60 parts of silica correspond with 40 parts of silicon carbide—SiC; hence, 30·71 parts of silica correspond with 20·47 parts of SiC. Again, 40 parts of silicon carbide correspond with 12 parts of carbon; hence, 20·47 parts of silicon carbide correspond with 6·14 parts of carbon as silicon carbide. Hence, 50·12 less 6·14 represents 43·98 per cent. of free carbon. The first two terms of the preceding analysis may now be revised. They read:

Silica	17·6
Silicon carbide	20·5
Carbon	44·0

The collected errors in the analysis are here distributed between the silica, silicon carbide, and the carbon, and the method can only be regarded as a method of approximation.

According to Parr,[2] the free silica is removed by evaporation with hydrofluoric acid, which does not attack silicon carbide—SiC. Hence, determine the total silicon by the fusion process, and the free silica in a separate sample by means of hydrofluoric acid. He expresses the analysis: silica (volatilised with HF), 8·27; metallic iron (removed by a magnet), 4·37; silicon as Si (by fusion process), 63·58; carbon (volumetric from fusion mixture, page 562), 23·67 per cent.

§ 295. The Analysis of Siloxicon.

Siloxicon is a greenish-grey refractory substance which varies in composition between Si_2C_2O and Si_7C_2O. It is vigorously decomposed, but not completely, by a fused mixture of sodium carbonate and potassium nitrate. Hydrofluoric and sulphuric acids have but a slight action. It is vigorously attacked by heated lead peroxide.[3] Spielmann[4] analysed a sample of the substance in the following manner:—

Silicon, Carbon, and Moisture.—The amount of moisture is determined, in the usual way, by drying the sample to a constant weight at 110°. The substance is "opened" by fusing the sample with sodium peroxide in a nickel crucible (page 266). The siloxicon is vigorously attacked, and the resulting cake, when cold, is digested in water, and then with dilute hydrochloric acid. The resulting solution is treated in the usual manner, and the amount of silica obtained is multiplied by 0·46932. This represents the amount of silicon—Si—in the given sample. The total carbon is determined by fusing the sample with sodium peroxide in an iron boat in a combustion tube in a gentle stream of oxygen. In one experiment a potash bulb was fitted to the tube to collect any carbon dioxide which might escape; but none did escape, and hence the carbon was afterwards estimated from the amount of carbonate in the product of the fusion of the siloxicon with the sodium peroxide in a crucible. The carbon dioxide in the fused mass was determined by the action of dilute sulphuric acid[1] in the usual manner (page 552).

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[1] It will be noted that we use rounded atomic weights. The resulting error is negligibly small in comparison with the approximate nature of the method of computation.

[2] S. W. Parr, *Journ. Amer. Chem. Soc.*, **30**. 764, 1908.

[3] P. Jannasch and H. J. Locke, *Zeit. anorg. Chem.*, **6**. 168, 321, 1894; A. Leclerc, *Compt. Rend.*, **125**. 893, 1897; P. Jannasch, *Zeit. anorg. Chem.*, **8**. 364, 1895; *Chem. News*, **72**. 51, 1895.

[4] P. E. Spielmann, *Journ. Soc. Chem. Ind.*, **24**. 654, 1905.

Alumina, Iron, and Si_2C_2O.—Another sample was heated in a stream of chlorine in a porcelain boat in a hard combustion tube, whereby silicon tetrachloride, ferric chloride, and a trace of aluminium chloride were volatilised. These were absorbed by passage (1) over the surface of water in a flask; and (2) through a U-tube loosely packed with cotton-wool. The silicon tetrachloride was hydrolysed to silicic acid. When all the ferric chloride had volatilised, the combustion tube was heated by the blast to as high a temperature as the tube would stand without squatting. The reaction is at an end when the contents of the boat cease to glow. The cotton-wool was burnt in a crucible, and the oxides of silicon and iron remained. The aluminium, iron, and silicon collected in the flask and by the cotton-wool were determined as usual. The residue in the boat was heated in a current of oxygen, and the carbon dioxide determined by absorption, etc., in potash bulbs. The residue in the boat was found to be almost pure Si_2C_2O.[2]

Calculations.—Spielmann collects his results in the following manner:

	Per cent.
Total silicon (Na_2O_2 fusion)	50·31
Total carbon (Na_2O_2 fusion)	31·39
Iron (heating in chlorine)	1·07
Aluminium (heating in chlorine)	trace
Moisture	0·19
	82·96
Oxygen (difference from 100)	17·04
Residue in boat (Si_2C_2O)	71·39
Carbon on heating chlorine residue in oxygen	11·79

The latter represents the carbon which occurred in siloxicon partly as graphite and partly as carborundum (decomposed by chlorine). This quantity, with the amount calculated for Si_2C_2O and subtracted from the total carbon, leaves 1·47 per cent. of carbon. The oxygen in Si_2C_2O subtracted from the total oxygen leaves 5·24 per cent. of oxygen. This, with the 1·47 per cent. carbon, is that required for $SiCO_3$. This amount of silicon subtracted from the silicon volatilised by the chlorine (7·54 per cent.) gives the amount of silicon present as carborundum, *i.e.* 4·08 per cent. The amount of carbon thus combined is 1·73 per cent. This subtracted from the weight of carbon burnt on oxygen leaves the amount of carbon present as graphite. Collecting these results together, the analysis reads:

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[1] If hydrochloric acid be used, some chlorine will be formed.

[2] A portion of the sample was boiled with hydrofluoric acid. The filtrate contained a trace of ammonium silicofluoride. This was probably due to the presence of a trace of silicon nitride in the original sample.

Si_2C_2O	71·39
$SiCO_3$	10·18
SiC (carborundum)	5·81
Graphite	10·06
Fe	1·07
Volatiles	0·19
Al_2O_3 ; Si_3N_4 (by diff.)	0·67

The method of calculation can only be regarded as the roughest of approximations.

§ 296. The Analysis of Graphite, and Graphite Crucibles.

If the sample has no chemically combined water, as is the case with some of the artificial graphites, the carbon can be simply determined by heating the dried sample in a capacious Rose's crucible fitted so that a current of dry oxygen can be passed into the crucible while the calcination is in progress. The loss in weight represents the graphite burnt.[1] With natural graphites, however, this method is risky, because some silicates may be present which lose water only at elevated temperatures. Again, if pyrites, FeS_2, be present, the sulphur is burnt to the dioxide, and ferric oxide is formed such that one part of pyrites furnishes two-thirds its weight of ferric oxide. If appreciable quantities of occluded oxygen, hydrogen, nitrogen, and sulphur be present, this method will give erroneous results.[2]

Berthier's old process[3] is not infrequently employed when rapid work is needed. 0·5 grm. of the finely powdered sample is intimately mixed with 12 grms. of powdered lead monoxide, and placed in an unglazed porcelain crucible. The surface of the mixture is covered with 12 more grms. of lead monoxide, and heated slowly. The lead monoxide is reduced by the carbon so that 1 grm. of reduced lead represents 0·03 grm. of graphite. Quite good results can be obtained by this process if care be exercised in selecting the lead monoxide, and if the sample be free from sulphides.

The sample can be readily powdered in a hardened steel mortar with a ball pestle (fig. 69), and finished in an agate mortar. The wet combustion process gives rather low results.[4] Hence, pack a hard glass combustion tube with an asbestos plug as indicated on page 563. Then fill about 45 cm. of the tube with granulated or wire copper oxide[5] instead of granulated lead oxide. Then insert another plug of the asbestos. Mix, say, 0·2 to 0·3 grm. of the powder with powdered copper oxide,[6] and transfer the mass to a porcelain boat. Place the boat in the combustion tube. Follow this with a roll of copper gauze, 13 cm. long, bound with copper wire arranged with a hook at one end. The roll should slide easily into the combustion tube, after the boat[1]—see fig. 177. The combustion is conducted as indicated on page 563.[2] When silicon carbides are absent, the loss on ignition,[3] silica, etc., can be determined as for clays.[4]

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[1] E. Donath, *Der Graphite*, Wien, 163, 1904. See also page 545, § 285.

[2] E. Donath, *Der Graphite*, Wien, 168, 1904 ; G. Auchy, *Journ. Amer. Chem. Soc.*, **22**. 47, 1900.

[3] P. Berthier, *Dingler's Journ.*, **58**. 391, 1835 ; *Traité des Essais par la Voie Sèche*, Paris, **1**. 222, 1847 ; W. F. Gintl, *Zeit. anal. Chem.*, **7**. 423, 1868 ; G. C. Wittstein, *Dingler's Journ.*, **216**. 45, 1875. G. Forchhammer (*Berg. Hütt. Ztg.*, **5**. 465, 1846) recommended a mixture of three parts of lead monoxide and one part of lead chloride in place of lead monoxide alone, because the former fuses at a lower temperature and does not corrode the crucible so much. A. Schrötter (*Dingler's Journ.*, **116**. 115, 1850) used lead oxychloride.

[4] J. Widmer, *Zeit. anal. Chem.*, **29**. 160, 1890 ; *Chem. News*, **62**. 274, 1890. J. Goldstein, (*Chem. Ztg.*, **35**. 1134, 1911) considers that the combustion with sulphuric and chromic acids in Corleis' flask, etc., page 546, gives best results.

[5] C. Reischauer, *Viert. prakt. Pharm.*, **11**. 38, 1862 ; E. C. C. Stanford, *Chem. News*, **7**. 81, 1863 ; E. Erlenmeyer, *Zeit. Pharm.*, **6**. 156, 1854.

[6] If the ash is liable to sinter, calcined magnesia or zinc oxide is mixed with it—S. S. Sadtler, *Journ. Franklin Inst.*, **144**. 201, 1907—otherwise particles of unburnt carbon may be sealed in the slag and thus protected from oxidation.

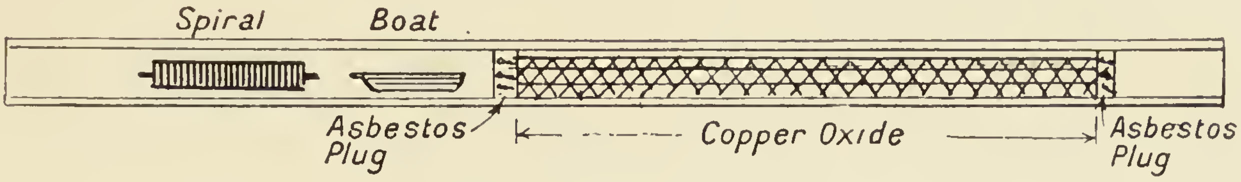

Fig. 177.—Diagrammatic sketch of combustion tube.

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[1] The copper gauze should be heated in a Bunsen's flame so as to burn off oil and combustible matters. E. Calberia (*Journ. prakt. Chem.* (1), **104**. 232, 1869) prefers silver gauze.

[2] The tube should be heated in a current of oxygen before the boat is introduced in order to burn out every particle of dust and moisture.

[3] F. Stolba, *Dingler's Journ.*, **198**. 213, 1870. Due allowance is of course made for the carbon.

[4] F. Mayer (*Chem. Ztg.*, **35**. 1024, 1911) estimates the amount of carbon in graphite from its calorific power.

CHAPTER XXXIX.

THE DETERMINATION OF WATER.

§ 297. Brush and Penfield's Method.

It is sometimes desirable to determine directly the amount of water evolved when clays and related materials are ignited, although the determination is seldom asked for in industrial work. Brush and Penfield[1] conduct the process in the following manner:—One or two bulbs are blown on a piece of hard glass combustion tube about 25 cm. long, with an internal diameter of about 0·6 mm., as shown in the diagram, fig. 178. Air is blown through the hot tube by means of a piece of glass tubing reaching nearly to the bottom of the combustion tube so that the tube may be thoroughly dried. Weigh the tube with its support.[2] Introduce about 0·5 grm. of the powdered sample by means of a kind of thistle funnel, *a*, fig. 179,[3] without soiling the tube away from the closed end. The

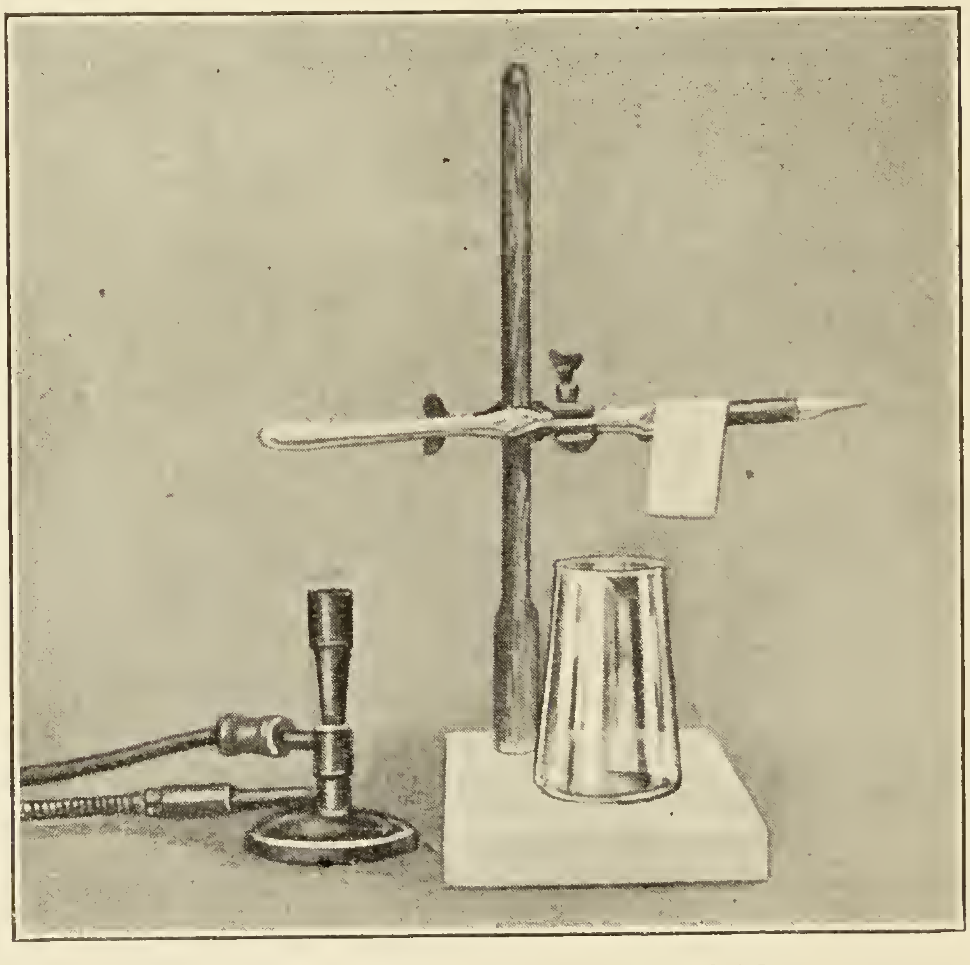

Fig. 178.—Determination of water—Penfield's process.

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[1] G. J. Brush, *Amer. J. Science* (1), **46**. 240, 1868; S. L. Penfield, *ib.* (3), **48**. 31, 1894; *Zeit. anorg. Chem.*, **7**. 22, 1894; F. A. Gooch, *Amer. Chem. Journ.*, **2**. 247, 1880; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 72, 1910. For a general study of the subject, see G. N. Huntley and J. H. Coste, *Journ. Soc. Chem. Ind.*, **32**. 62, 1913.

[2] For a brass "tube support" for steadying the tube on the pan of the balance, see fig. 3*a*.

[3] Can be made from a small pipette.

powder should occupy 2 or 3 cm. of the tube. Weigh the tube, support, and sample together. Take care not to roll the powder in the tube towards the bulbs.[1] The open end of the tube may be fitted with a piece of rubber tube holding a glass tube drawn out to a capillary end, *b*, fig. 180. Tap the tube so as to form a free passage for steam, etc., above the powder. Support the tube with a very slight slope downwards from the closed end; wrap a strip of filter paper or cloth about the bulb and tube near the open end—fig. 178. Keep the filter paper moist and cold so as to ensure condensation of the moisture expelled from the powder. The powder is now heated gradually up to the full heat of the burner. If the heated end tends to sink, turn the tube around from time to time.[2] In about 15 minutes, drive the water in the tube a safe distance from the closed end, and seal off the part containing the water by means of a blowpipe flame. Let this portion of the tube cool in a horizontal position. Wipe the outside clean, and weigh. Blow the steam and moisture from the other tube by placing a small tube inside the larger one and reaching to the bottom. The loss in weight represents the total moisture.

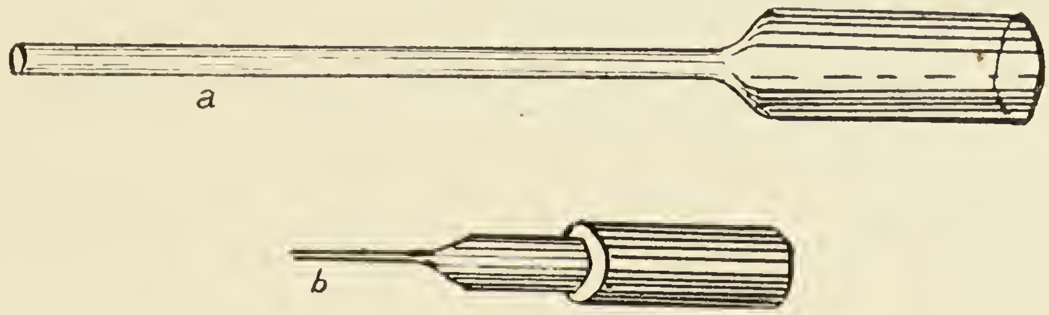

FIG. 179.

The weighings, etc., are made as indicated in the following example:

Weight of tube plus powder	69·9214 grms.
Weight of empty tube	69·4321 grms.
Weight of powder	0·4893 grm.
Weight of portion containing water	20·8142 grms.
Weight after expulsion of water	20·7997 grms.
Weight of water	0·0245 grm.

Hence the sample contained 5·01 per cent. of water.

§ 298. Jannasch's Process for Water.

Jannasch[3] determines the moisture in the presence of sulphur, fluorine, etc., by fusing the substance with about six times its weight of lead oxide and collecting the water evolved in calcium chloride tubes. The other gases are said to be retained by the lead oxide. A hard glass tube, 26 cm. long, with an internal diameter of 1 cm., has a long bulb, *A*, blown about 11 cm. from one end. The bulb must have thick walls, and the whole tube thoroughly dried. In fig. 180, *b b* are plugs of glass-wool; *c*, a loosely packed layer of PbO_2 and PbO (page 547) about 5 cm. long. The object of the lead oxides is to retain the chlorine, fluorine, sulphur, etc. This part of the tube must be kept hot while an experiment is in progress. One end of this tube is fitted with a calcium chloride tube *B*, and potash bottles *H H*; the opposite end is fitted with a calcium chloride tube (page 561) *C*; a potash bulb *D* with its calcium chloride tube *E*; guard tube *F*; and aspirator *G*. The object of the potash bottles *H H*, and calcium chloride tube *B*, is to remove moisture and carbon dioxide from the aspirated air (page 567).

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[1] If the sample has not been dried, it may now be dried at, say, 109°, and the system weighed again for "water lost at 109°."

[2] For minerals like talc which do not give up all their water even when blasted, Penfield uses a cylinder of platinum foil (about 0·07 mm. thick) sprung tightly inside the part of the glass tube which is to be heated intensely, so as to prevent the glass squatting. The outside of the tube is surrounded with a piece of asbestos board. The end of the tube to be heated is partly surrounded with blocks of charcoal and fireclay so arranged that the tube is in a small furnace, which, later on, can be heated by a blast gas blowpipe.

[3] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 357, 1904; P. Jannasch and P. Weingarten, *Zeit. anorg. Chem.*, 8. 352, 1895; P. Jannasch and J. Locke, *ib.*, 6. 168, 1894; M. Dittrich and W. Eitel, *ib.*, 75. 373, 1912; *Sitzber. Heidelberger Akad. Wiss.*, 19, 1911; W. Eitel, *Die Bestimmung des Wassers in Silikat-Mineralien und Gesteinen*, Frankfurt a. M., 1912.

From 0·5 to 1 grm. of the powder is mixed with six times its weight of lead monoxide[1] on glazed paper, and the mixture is transferred to the middle of the bulb by means of a long strip of glazed paper and a feather. The operation requires care. No powder must be lost, and none left sticking to the sides of the tube.[2]

Now raise the temperature of the bulb and contents gradually, and finally finish the ignition at a full red heat. The calcium chloride absorbs the water;[3] the potash, the carbon dioxide. After about 10 minutes' ignition the reaction should be completed. Let the tube cool in a current of dry air freed from carbon dioxide. The tube *C* and the set of bulbs *DE* are then weighed. The increases in weight in the respective tubes represent the absorbed water and carbon dioxide.

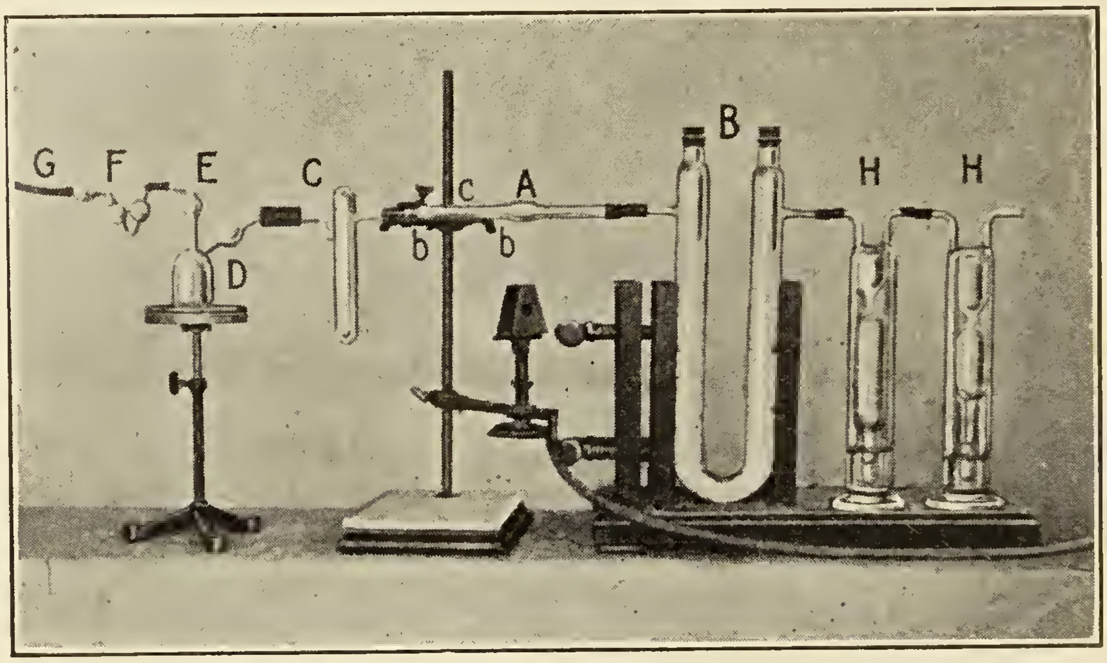

FIG. 180.—Direct determination of water.

The simultaneous determination of carbon or carbon dioxide and moisture has been discussed on pages 562–4. Assuming that the hygroscopic moisture has been expelled by drying the sample at 110°, a certain proportion of the remaining water in carbonaceous clays will be derived from the clay; and the remainder, from the organic matter. In that case, digest a weighed portion of the sample with a mixture of two volumes of fuming hydrofluoric acid and one volume of hydrochloric acid (sp. gr. 1·18); evaporate to dryness. Repeat the operation three times. Digest the residue with hot water, filter through an asbestos-packed Gooch's crucible or carbon tube, wash, and dry at 110°. After weighing, the carbon may be detached from the filter and the ratio of carbon to hydrogen determined by combustion of the organic matter to carbon dioxide and water.[1] Jannasch's process or one of the methods indicated in the preceding chapter may be used for the combustion.

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[1] Freed from carbon dioxide by heating in a porcelain tube.

[2] For the amount of moisture which calcium chloride, sulphuric acid, and phosphoric oxide leave in a gas, see page 156.

[3] E. Ludwig, *Tschermak's Mitt.* (1), **2**. 214, 1875; *Zeit. anal. Chem.*, **17**. 206, 1878; L. Sipöcz, *ib.*, **17**. 207, 1878; *Sitzber. K.K. Akad. Wiss. Wien*, **86**. 51, 1877. The former used a platinum tube; the latter, a platinum boat.

EXAMPLE.—A carbonaceous clay gave the following percentage results:—

Jannasch's process	Total water	14·21
Lissner's process	Total organic matter	4·32
Combustion process	Carbon (calculated from CO_2)	4·16
	Hydrogen (calculated from H_2O)	0·10
	Organic matter	4·26

Hence, 4·26 [2] grms. of organic matter have 4·16 grms. of carbon, and 0·10 grm. of hydrogen. But 0·10 grm. of hydrogen corresponds with 0·90 grm. of water. Hence, the sample of clay contained :

Water	13·31 per cent.
Organic matter	4·32 per cent.

These numbers can only be regarded as an approximate representation of what they are supposed to designate.

According to Danne,[3] the amount of moisture can be determined in many substances by heating them with calcium carbide, and measuring the volume of acetylene obtained. The method has been extended to the determination of the "water of crystallisation" in many salts. The method has also been modified by allowing the acetylene to escape, and estimating the water from the loss in weight of the apparatus owing to the escape of acetylene.

§ 299. Fractional Dehydration: Water lost at Different Temperatures.

Some zeolites, and hydrated alumino-silicates, give off water [4] below 110°, and in that case the clay can be heated at, say, 100°, 110°, 120°, 130°, . . . to find if the substance loses appreciable amounts of water at progressively higher temperatures. The results are then represented as "water below 100°," "water between 100° and 110°," etc. When the water is to be determined at different temperatures in this manner, a copper cylinder is fitted up as shown in fig. 181 with a thermostat, *A*, and thermometer, *B*. The glass tube, say 30 cm. long and 3·5 or 4 cm. wide, has a hollow stopper ground at one end *C*; the stopper is fitted with a tube and stopcock, *C*. The other end of the glass tube is drawn out and fitted with a drying tower, *E*.

The copper cylinder has an outer jacket of asbestos. The glass tube is plugged in the copper tube with carded asbestos. The thermostat is regulated to keep the furnace at the desired temperature any length of time. Hence, any material placed in a small squat uncovered weighing bottle resting in the glass tube can be heated to any desired temperature while a current of air is drawn through the apparatus. The air is dried by passing it through a drying tower at the end *E*. This tube is packed with soda lime and calcium chloride, the former to remove carbon dioxide, the latter, moisture. A weighed calcium chloride tube, *F*, is placed at the end *C* to absorb any moisture driven from the substance in the weighing bottle. The increase in weight of this tube during an experiment represents the moisture driven from the substance. The result may be checked by also weighing the loss of weight of the weighing bottle. The two may not necessarily coincide, since volatile substances other than water may be driven off. The small bulbs *g* contain sulphuric acid. This tube shows the rate at which air is passing through the apparatus, by counting the number of bubbles per second.

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[1] A. Lissner, *Chem. Ztg.*, **34**. 37, 1910. See page 521.

[2] The difference between 4·32 and 4·26 represents analytical errors, or oxygen, nitrogen, etc.

[3] H. A. Danne, *Proc. Soc. Chem. Ind. Victoria*, 1900; P. V. Dupré, *Analyst*, **30**. 266, 1905; **31**. 213, 1906; R. A. Cripps and J. A. Brown, *ib.*, **34**. 519, 1909; R. W. Roberts and A. Frazer, *Journ. Soc. Chem. Ind.*, **29**. 851, 1910; F. H. Campbell, *ib.*, **32**. 67, 1913; I. Masson, *Journ. Chem. Soc.*, **97**. 851, 1910; *Chem. News*, **103**. 37, 1911; A. C. D. Rivett, *ib.*, **104**. 261, 1911; H. C. McNeil, *Chem. Eng.*, **16**. 38, 1912.

[4] For the gases in silicates, see A. P. Lidoff, *Zeit. anal. Chem.*, **46**. 357, 1907; R. T. Chamberlain, *The Gases in Rocks*, Washington, 1908.

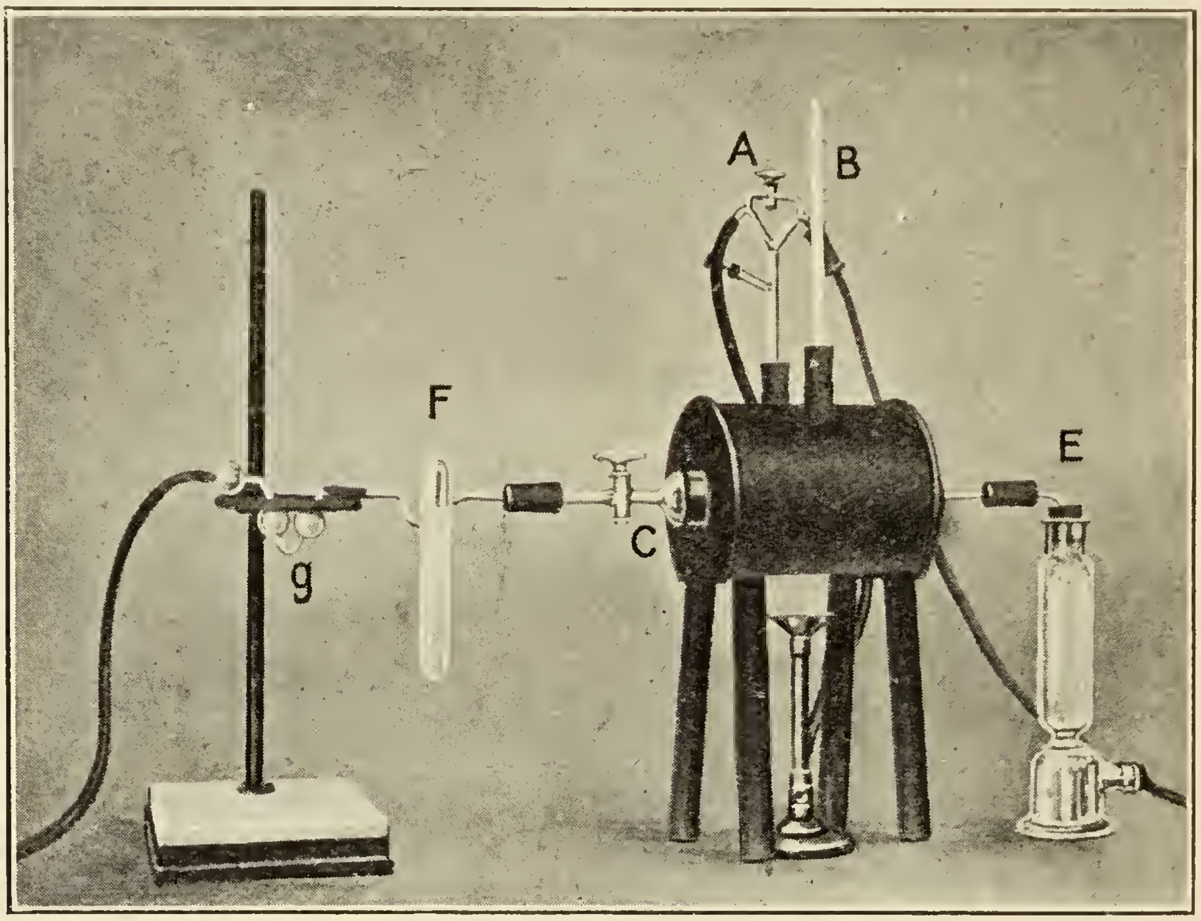

Fig. 181.—Fractional dehydration.

If the cock *C* be closed, and the other end connected with a suction pump, the substance can be heated under reduced pressure. In that case, the tube *F* is fitted to the opposite end of the glass tube.[1]

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[1] J. W. Mellor (*Trans. Eng. Cer. Soc.*, 7. 114, 1908; J. W. Mellor and A. D. Holdcroft, *ib.*, 11. 1, 1911) describes a method for heating the tube electrically at any desired temperature. If the joints of the furnace in the preceding diagram be brazed, and the thermostat, *A*, replaced by a reflux condenser, liquids whose boiling points are known can be employed. For instance:

Table LXIV.—Liquids for Vapour-Baths.

Liquid.	Temperature available.	Price per lb.
Benzene	80–81°	7d.
Water	99–100°	
Toluene	109–112°	9d.
Ethyl butyrate	120–121°	1s. 6d.
Amyl alcohol	128–132°	1s 7d.
Xylene	139–141°	8d.
Cumene	152–153°	1s. 5d.
Pseudocumene	165–168°	1s. 2d.
Salol	172–173°	3s. 0d.
Aniline	180–182°	11d.
Dimethylaniline	191–193°	3s. 5d.
Nitrobenzene	207–209°	11d.

The temperature of the inner chamber is generally 2° to 5° lower than the boiling point of the liquid in the outer chamber.

Guttmann's[1] weighing bottle, fig. 182, is useful for heating substances to a constant weight in a current of gas, and hence determining the loss in weight on heating to different temperatures. The gas entry and exit tubes have ground caps for protecting the contents from air during the weighing.

Meyer's[2] vapour bath or oil bath is useful when a small amount of a substance is to be heated to a given temperature below about 200°. The bath is shown in section in fig. 183. A porcelain cylinder is placed inside a double-walled copper cylinder. The crucible containing the substance under investigation is placed in the inner cylinder. A suitable liquid is placed in the copper vessel. The latter is fitted with a condenser, *C*. A small flame and a small amount of liquid are needed for the work. For temperatures higher than 200°, oils may be used. A current of air circulates outside the inner cylinder, entering at *a* and leaving at *b*.

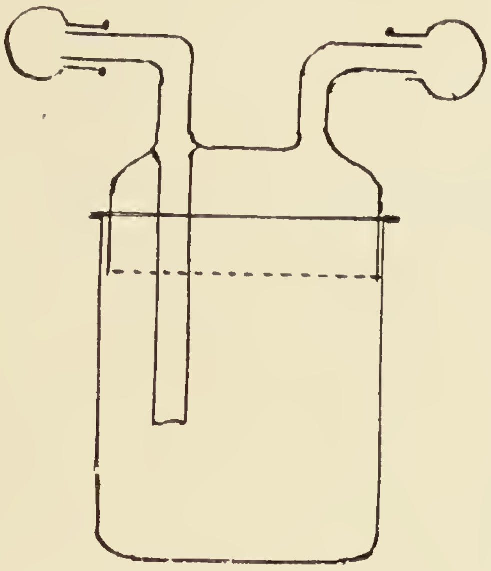

FIG. 182.—Guttmann's weighing bottle.

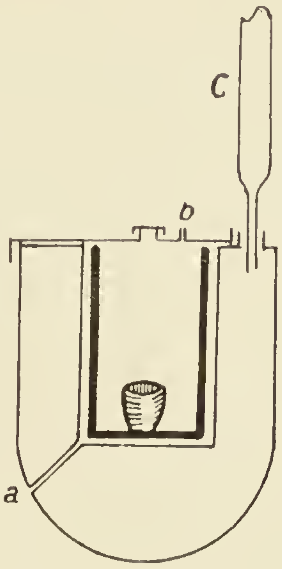

FIG. 183.—Meyer's vapour bath.

It seems fairly certain that some clays lose more moisture when dried under reduced pressure over sulphuric acid[3] than when they are heated to constant weight in the hot oven, fig. 90, page 156. Skertchly[4] has shown that many organic substances do the same thing.

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[1] L. F. Guttmann, *Journ. Amer. Chem. Soc.*, 28. 1667, 1906.
[2] V. Meyer, *Ber.*, 18. 2999, 1885 ; A. Fock, *ib.*, 18. 1124, 1885.
[3] E. Löwenstein, *Zeit. anorg. Chem.*, 63. 69, 1909.
[4] W. P. Skertchly, *Journ. Soc. Chem. Ind.*, 32. 70, 1913.

CHAPTER XL.

THE DETERMINATION OF BORON.

§ 300. The Detection of Boric Oxide.

The following remarks on this subject supplement those given in the regular text-books on qualitative analysis. It is generally necessary to get the borate in a soluble condition. This is done by fusing the borosilicate with five to ten times its weight of sodium carbonate, and extracting the cold mass with water.

The Alcohol Flame Test.—Boric acid dissolves in alcohol, and the alcohol burns with a flame tinged with green. Similarly, if a borate be decomposed by treatment with an acid,[1] and the mass be mixed with alcohol, the alcohol, when ignited, burns with a greenish flame. The test is carried out by igniting the mixture on a watch-glass.[2] It is possible to detect 0·001 per cent. of boric oxide in a solution by the flame test, and a glaze containing 0·1 per cent of boric oxide will give a distinct reaction.

If copper be present, the test is not satisfactory. The copper must be first removed by hydrogen sulphide. Barium salts also colour the flame green. If sulphuric acid be used to decompose the borate, non-volatile barium sulphate is formed, and barium does not then interfere with the test. When copper or barium is present, the flame test is best made by placing the mixture in a six-inch test tube fitted with a cork and gas-jet as illustrated in fig. 184. The test tube is heated, and when the alcohol begins to boil, light the flame with a second burner. The copper and barium do not then interfere. If metallic chlorides be present, ethyl chloride may be formed, and this colours the flame green, thus spoiling the test. This difficulty is easily avoided by using sulphuric or nitric acid, not hydrochloric acid.

The Glycerol Flame Test.[3]—The powdered and calcined borate is moistened with sulphuric acid and heated on a platinum foil until the acid is expelled. Moisten the mass with glycerol. The glycerol burns with a green flame if boric oxide be present. The glycerol test will indicate 0·001 per cent. of boric oxide. For the disturbing agents, see the alcohol flame test.

Turmeric Test.—If a borate be just acidified with dilute hydrochloric acid, and a strip of turmeric paper[4] be half immersed in the solution, no apparent change occurs; but if the paper be dried on a watch-glass at 100°, the half which has been dipped in the boric acid shows a peculiar brownish-red coloration. If but a small trace of boric oxide be present, the stain may be pink. The colour remains when the stain is dipped in boric acid again, or in dilute sulphuric or hydrochloric acid. The brown stain produced by alkalies changes into yellow under these conditions. If too little acid be used, there may be no coloration; if too much, the colour may be brown. If the boric acid stain be touched with a solution of potassium hydroxide, the paper becomes bluish black or bluish grey, according as much or little boric acid be present. A little hydrochloric acid will restore the red colour. As little as 0·0001 grm. of boric acid can be detected by the (pink) colour produced in this manner. The presence of oxidising agents like chlorates, chromates, iodides,[1] etc., interferes with the test by destroying the turmeric. Nitric acid is an exception. Concentrated hydrochloric acid may give a dark brown stain under the conditions of the test; ferric chloride, molybdenum and zirconium salts give a brownish-red stain which is not coloured bluish black with potash solution.

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[1] The borate is supposed to be decomposable by treatment with acids—sulphuric, hydrochloric, or hydrofluoric acids; or by a mixture of ammonium nitrate and chloride; sulphuric and hydrochloric acid; or sulphuric and nitric acid.

[2] H. Bornträger, *Zeit. anal. Chem.*, **39**. 92, 1900; M. Bidaut, *Compt. Rend.*, **76**. 489, 1873; **80**. 387, 1878; M. Dieulafait, *ib.*, **85**. 605, 1877; *Ann. Chim. Phys.* (5), **12**. 318, 1877.

[3] M. W. Iles, *Amer. Chem.*, **6**. 361, 1876; H. Gilm, *Ber.*, **11**. 712, 1878.

[4] Turmeric paper gives a brownish colour with alkalies, yellow with acids.

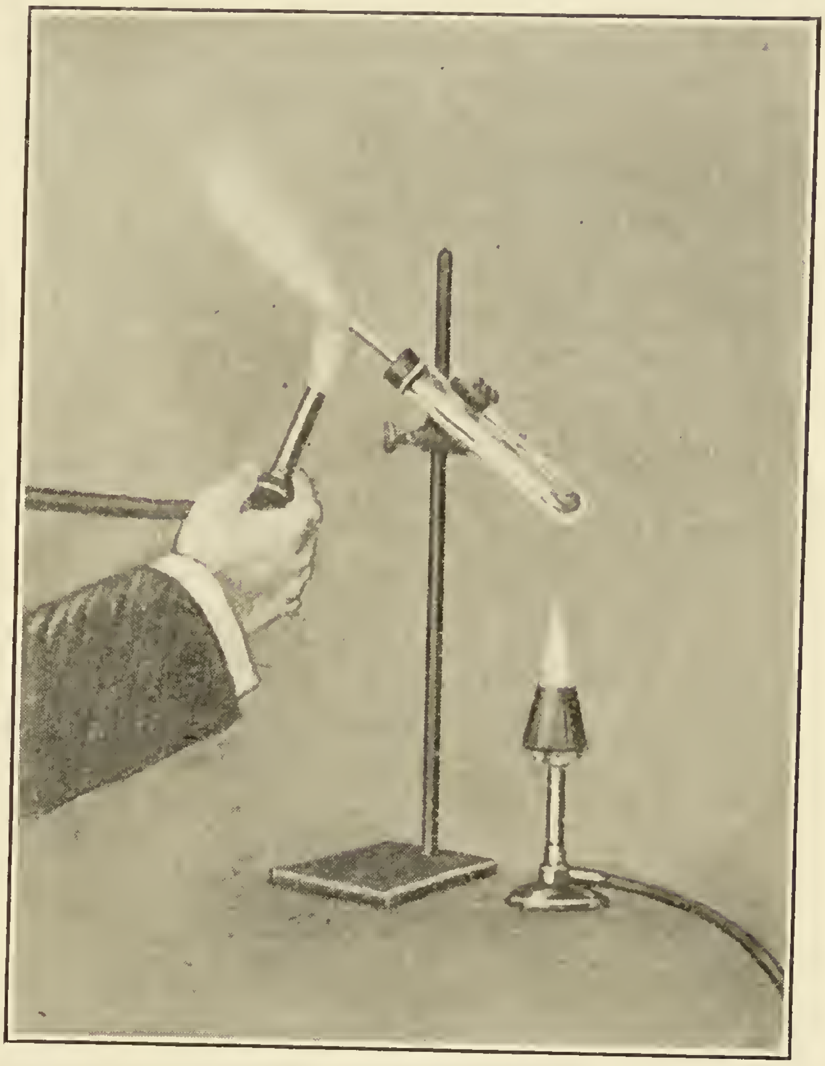

FIG. 184.—Flame test for boric oxide.

Still smaller amounts of boric oxide can be detected if needed by placing the solution under investigation in a small dish and evaporating it to dryness in a desiccator *in vacuo* at a low temperature. If a few drops of an alcoholic extract of a few turmeric papers be mixed in a porcelain dish with the borate, the solution acidified with acetic acid, and evaporated to dryness on a water bath, a reddish-brown residue will be obtained if as little as 0·0002 grm. of B_2O_3 be present, while 0·00002 grm. will produce a perceptible coloration.[2]

The Boron Fluoride Test.—If the powdered borate be mixed with a few drops of water and approximately three times its weight of Turner's flux,[3] and the paste be exposed on the loop of a platinum wire in the outer mantle of Bunsen's flame, the boron fluoride which is formed imparts a greenish tinge to the flame. The reaction will detect 0·01 per cent. of B_2O_3 in a silicate.[4]

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[1] Chlorates and chromates may be reduced by treating the solution with solid sodium sulphite; add hydrochloric acid, and warm the solution to drive off the excess of sulphurous acid. Filter if necessary, and boil the filtrate with a slight excess of sodium carbonate, dilute, and filter. Iodides, if present, may be removed by precipitation with silver nitrate in a solution acidified with nitric acid. The addition of 5 grms. of urea per 100 c.c. of solution inhibits effects of nitrites; nitrates do not interfere—T. M. Price and E. H. Ingersoll, *Bull. U.S. Dept. Agric. (Chem.)*, **137**. 115, 1912.

[2] M. Ripper, *Weinbau Weinhandl.*, **6**. 331, 1888; P. Kulisch, *Zeit. angew. Chem.*, **7**. 187, 1894; V. Lehner and J. S. C. Wells, *Journ. Amer. Chem. Soc.*, **21**. 417, 1894; H. Bornträger, *Zeit. anal. Chem.*, **29**. 92, 1900; W. H. Low, *Journ. Amer. Chem. Soc.*, **28**. 807, 1907.

[3] TURNER'S FLUX.—Mix finely powdered calcium fluoride or potassium fluoride with 4·5 times its weight of potassium bisulphate. Hydrofluosilicic acid may be used in place of this flux if the borate is easily decomposed.

[4] E. J. Chapman, *Chem. News*, **35**. 12, 26, 36, 1877; C. le Neve Foster, *ib.*, **35**. 127, 1877; H. Kämmerer, *Zeit. anal. Chem.*, **12**. 376, 1873.

§ 301. The Determination of Boric Oxide.

In 1851, Rose[1] stated that the quantitative determination of boric oxide was so very difficult that up to that time no method had been devised which gave a direct result. The problem has since been solved, but the process is difficult and laborious. Rosenbladt[2] thinks this "one of the most complicated operations in analytical chemistry." Vogt[3] estimated the boric oxide in silicates by difference after the other constituents had been determined. This method is not recommended. Several indirect methods have been proposed.[4] The isolation of a definite compound of boric oxide from the associated constituents is a necessary preliminary for the successful determination of boric oxide. The removal of silica and alumina is particularly difficult. Ferric oxide and alumina, for instance, when precipitated by ammonia carry down some boric oxide.[5] The silica also is difficult to separate without loss of boric oxide, because, if the mixture be treated with hydrofluoric and sulphuric acids in the usual manner, boron is volatilised as boron fluoride. Hence, silica may contaminate the compound of boron which is finally weighed.[6] Before dealing with complex silicates, it will be convenient to take simpler problems; and first, the volumetric determination of boric oxide in boric acid.

Volatilisation of Boric Oxide and Borax.—At the outset it is necessary to emphasise the fact that the substances now under investigation are somewhat volatile. For example, there is a difficulty in drying boric oxide, since a comparatively large amount of boric acid is lost. For instance, the loss of boric oxide on driving off the water of crystallisation from 1 grm. of boric acid containing

Water . . .	0·7808	0·7543	0·7492	0·7544	0·2885	0·2780	0·2783	grm.
B_2O_3 lost . . .	0·1405	0·1358	0·1449	0·1508	0·0896	0·1034	0·1032	grm.

during the expulsion of the water.[7]

Aqueous solutions containing boric acid, or solutions of borax acidified with sulphuric or hydrochloric acid, lose much boric acid when evaporated. In illustration, some of Tschijewski's experiments might be quoted. Solutions containing

B_2O_3	0·6030	0·2638	0·1268	0·0323	0·0314	0·0095	grm.
B_2O_3 lost	0·0522	0·0298	0·0278	0·0123	0·0114	0·0071	grm.

on evaporation to dryness on a water bath.[8]

Borax also during calcination loses boric oxide. Thus, Waldbott[9] found that when 0·6532 grm. of borax glass was blasted for

Time . . .	5	12	22	29	39	44	46	minutes.
Loss . . .	0·8	1·0	2·0	2·5	3·3	4·1	4·2	per cent.

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[1] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2.** 721, 1851.

[2] T. Rosenbladt, *Zeit. anal. Chem.*, **26.** 18, 1887.

[3] G. Vogt, *Ber. Internat. Kongress angew. Chem.*, **5.** i, 738, 1904 ; H. Rose, *l.c.*

[4] A. Arfvedson, *Schweigger's Journ.* (2), **8.** 1, 1802 ; F. G. Schaffgotsch, *Pogg. Ann.*, **107.** 427, 1859 ; J. J. Berzelius, *ib.*, **2.** 118, 1824 ; H. Rose, *ib.*, **80.** 261, 1850 ; K. Kraut, *Zeit. anal. Chem.*, **1.** 73, 1863.

[5] F. Wöhler, *Liebig's Ann.*, **141.** 268, 1867.

[6] *E.g.* in A. Stromeyer's process (*Liebig's Ann.*, **100.** 82, 1856) every one part by weight of silica contaminating the final precipitate quadruples the calculated amount of boric oxide.

[7] P. Tschijewski, *Arch. Phys. Nat.* (3), **12.** 120, 1884 ; *Bull. Soc. Chim.* (2). **42.** 324. 1884 ; H. Lescœur, *Ann. Chim. Phys.* (6), **19.** 43, 1890 ; L. Kahlenberg and O. Schreiner, *Zeit. phys. Chem.*, **20.** 547, 1896 ; F. W. Skirrow, *ib.*, **37.** 84, 1901 ; R. Bunsen, *Liebig's Ann.*, **111.** 257, 1859 ; G. Watson, *Chem. News*, **68.** 199, 1893 ; O. Hehner, *Analyst*, **16.** 141, 1891.

[8] L. de Koningh, *Journ. Amer. Chem. Soc.*, **19.** 385, 1897 ; F. G. Schaffgotsch, *Pogg. Ann.*, **107.** 427, 1859 ; J. A. Rose, *Beiträge zur Kenntnis der Borsäure und über eine direkt gewichtsanalytische Bestimmung derselben*, Bonn a. Rh. (Erlangen), 1902.

[9] S. Waldbott, *Journ. Amer. Chem. Soc.*, **16.** 410, 1894 ; E. Cramer, *Toniud. Ztg.*, **16.** 155, 1892. See page 589.

Starting with 2·1320 grms., 10 minutes' calcination over an ordinary Bunsen's burner gave no loss; 15 minutes over a moderate blast, with the crucible half covered, gave a loss of 0·0014 grm.; and over a strong blast, with the crucible open, 0·0073 grm. was lost. In a pottery oven, fired to Seger's cone 9 (scheduled 1280°) for

Time	60	48	26	3	hours.
Loss	48·98	22·40	7·88	1·47	per cent.

Hence boric oxide may also be lost when the "loss on ignition" is determined.

§ 302. The Evaluation of Boric Acid.

An aqueous solution of boric acid can be titrated with a standard solution of sodium hydroxide. Unfortunately, owing to the feeble acidic properties of this acid, the pink colour of the indicator, phenolphthalein, is developed before all the boric acid is neutralised. If, however, the solution contains sufficient glycerol, or mannitol,[1] the boric acid all reacts with the sodium hydroxide to form sodium metaborate:

$$NaOH + H_3BO_3 = 2H_2O + NaBO_2$$

before the pink of phenolphthalein appears. The polyhydric alcohol augments,[2] so to speak, the acidic qualities of the acid in question.

Thomson[3] has a process for the volumetric determination of boric acid based on these phenomena. Dissolve, say, 7·5 grms. of the boric acid in about 350 c.c of water in a 500-c.c. flask, and make the solution up to the 500-c.c. mark with water. Pipette 50 c.c. into an Erlenmeyer's flask; add 50 c.c. of glycerol,[4] or a gram of mannitol, and titrate with approximately $\frac{1}{2}$N-sodium hydroxide solution free from carbonates,[5] using phenolphthalein as indicator.[6] When the pink colour appears, add 10 c.c. of glycerol, or another gram of mannitol. If the pink colour disappears, continue the titration with the sodium hydroxide. Repeat the addition of glycerol or mannitol and titration until the pink colour persists when more mannitol or glycerol is added.

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[1] D. Klein, *Bull. Soc. Chim.* (2), **1.** 195, 1878; *Compt. Rend.*, **46.** 826, 1878; **99.** 144, 1884; M. Copaux, *ib.*, **127.** 756, 1898; A. Lambert, *ib.*, **108.** 1016, 1889; A. Senier and J. G. Lowe, *Pharm. Journ.* (3), **8.** 819, 1878; W. R. Dunstan, *ib.* (3), **13.** 257, 1882; R. Sulzer, *Deut.-Amer. Apoth. Ztg.*, 596, 1886; K. Jehn, *Arch. Pharm.* (3), **25.** 250, 1887; (3), **26.** 495, 1888; E. Donath, *Chem. Ztg.*, **17.** 1826, 1893; E. H. Farrington, *Rev. Internat. Falsif.*, **10.** 81, 1897; G. Deniges, *Journ. Pharm. Chim.* (6), **6.** 49, 1897; V. Gasselin, *Ann. Chim. Phys.* (7), **3.** 1, 1884; C. Schwarz, *Pharm. Ztg.*, **32.** 562, 1894; N. Tananaeff and D. Tsukerman, *Journ. Russ. Phys. Chem. Soc.*, **41.** 1469, 1910.

[2] K. Farnsteiner, *Zeit. Untersuch. Nahr. Genuss.*, **5.** 1, 1902; A. Beythein and H. Hempel, *ib.*, **2.** 842, 1899; B. Fischer, *ib.*, **3.** 17, 1900; G. Magnanini, *Rendi Accad. Lincei*, **6.** 260, 1890; *Gazz. Chim. Ital.*, **20.** 441, 448, 1890; **21.** ii. 134, 1891; *Zeit. phys. Chem.*, **6.** 58, 1890; L. Kahlenberg and O. Schreiner, *ib.*, **20.** 547, 1896; W. Vaubel and E. Bertlet, *Chem. Ztg.*, **29.** 629, 1905; A. Wogrinz and J. Kittel, *Chem. Ztg.*, **36.** 433, 1912.

[3] R. T. Thomson, *Journ. Soc. Chem. Ind.*, **12.** 432, 1896; *Analyst*, **21.** 64, 1896; A. H. Allen and A. R. Tankard, *ib.*, **29.** 301, 1905; L. Barthe, *Journ. Pharm. Chim.* (5), **29.** 163, 1894; M. Vadam, *ib.* (6), **8.** 109, 1898; M. Hönig and G. Spitz, *Zeit. angew. Chem.*, **9.** 549, 1896; G. Jorgensen, *ib.*, **10.** 5, 1897; N. Tananaeff and D. Tsukerman, *Journ. Russ. Phys. Chem. Soc.*, **41.** 1469, 1909.

[4] GLYCEROL SOLUTION.—Glycerol, 10, water 1, by volume. The glycerol must be free from fatty acids, or the fatty acids must be neutralised just before use with $\frac{1}{10}$N-sodium hydroxide solution. Glycerol usually becomes acid on keeping, possibly owing to the slow decomposition of fatty impurities.

MANNITOL (M. Vadam, *Chem. News*, **78.** 271, 1898; L. C. Jones, *Amer. J. Science* (4), **7.** 127, 1899; *Chem. News*, **80.** 65, 1899) is more convenient than glycerol. It is solid, easily handled, does not alter the bulk of the solution, and is not so liable to contamination with acids. The end point is also a little sharper. The results are quite as accurate as with glycerol. The choice is therefore a matter of convenience.

[5] Carbonates interfere with the indicator and react: $2B_2O_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2$. Hence, a little barium hydroxide is sometimes added during the preparation of the sodium hydroxide solution. See discussion, page 65. F. P. Venable and J. S. Callison (*Chem. Ztg.*, **14.** 167, 1890) report as much as 0·06 per cent. of boric oxide in caustic soda and caustic potash sold as "pure." M. Gorges, *Journ. Pharm. Chim.* (6), **3.** 346, 1896.

[6] Other indicators have been recommended: litmus (J. L. Gay Lussac, *Ann. Chim. Phys.* (2), **40.** 398, 1830), lacmoid (R. T. Thomson, *Chem. News*, **47.** 123, 135, 1883), congo red

EXAMPLE.—23·7 c.c. of the $\frac{1}{2}$N-solution of sodium hydroxide were required for a titration. This solution contains 20·004 grms. of NaOH per litre, which, according to the equation : $NaOH + H_3BO_3 = 2H_2O + NaBO_2$, corresponds with 31·01 grms. of H_3BO_3 per litre, or 1 c.c. of the standard solution is equivalent to 0·031 grm. of H_3BO_3. Hence, 23·7 × 0·031 = 0·735 grm. of H_3BO_3 per 50 c.c. ; or 14·69 per 1000 c.c. ; or per 15 grms. of the sample. Hence, the sample has 97·9 per cent. H_3BO_2.

Will and Zschimmer[1] titrate the boric acid with baryta water ; Smith[2] adds standard manganese sulphate and titrates with standard potassium permanganate ; and Jones[3] liberated iodine from a mixture of potassium iodide and iodate in presence of boric acid and mannitol, and determined the iodine by titration with sodium thiosulphate.

§ 303. The Evaluation of Borax.

Solutions containing boric acid are neutral to *p*-nitrophenol, and to methyl orange, but acid towards phenolphthalein—particularly in the presence of mannitol or glycerol. Hence, if hydrochloric acid be added to an aqueous solution of borax, using *p*-nitrophenol or methyl orange as indicator,[4] the solution will react acid only when all the boric acid is free and all the soda is neutralised by the hydrochloric acid. The reaction is represented :

$$Na_2B_4O_7 + 5H_2O + 2HCl = 2NaCl + 4H_3BO_3.$$

The boric acid can then be titrated as just indicated under boric acid. The determination is made in the following manner :—

Dissolve 10 grms. of borax in about 300 c.c. of water, and make the solution up to 500 c.c. with distilled water freed from carbonates by boiling. Titrate 25 c.c. with approximately $\frac{1}{2}$N-hydrochloric acid, using a drop of *p*-nitrophenol or methyl orange as indicator. Note the volume of hydrochloric acid needed for the neutralisation of the 25 c.c. pipetted from the main solution. Add the same volume of the standard hydrochloric acid to another 25 c.c. of the borax solution, add glycerol or mannitol as indicated under boric acid, and titrate, as there described, with, say, $\frac{1}{2}$N-sodium hydroxide, using phenolphthalein as indicator.

EXAMPLE.—10 grms. of the sample made up to 500 c.c. Of this, 100 c.c., that is, 2 grms. of the sample, required 42 c.c. of the standard hydrochloric acid, and 45·6 c.c. of the standard sodium hydroxide solution, 1 c.c. of which corresponded with 0·0437 grm. of crystalline borax. Hence, 2 grms. of the sample had 45·6 × 0·0437 = 1·992 ; or 99·6 per cent. of crystalline borax. A similar procedure is employed for anhydrous borax.

(C. Schwarz, *Pharm. Ztg.*, **37**. 562, 1887), helianthine (F. Parmentier, *Compt. Rend.*, **113**. 41, 1891), orceine (M. de Luynes, *Ann. Chim. Phys.* (4), **6**. 184, 1865), hæmatoxyline (A. Guyard, *Bull. Soc. Chim.* (2), **40**. 422, 1883), Porrier's blue (R. Engel, *ib.* (2), **45**. 327, 1886 ; *Compt. Rend.*, **102**. 214, 262, 1886), tincture of red rose leaves (L. Barthe, *Journ. Pharm. Chim.* (5), **29**. 163, 1894), tincture of mimosa blossoms (L. Robin, *Ber. Internat. Cong. App. Chem.*, **8**. i, 429, 1912).

[1] H. Will, *Arch. Pharm.*, **225**. 1101, 1887 ; R. Hefemann, *Pharm. Centr.* (2), **9**. 116, 1888 ; E. Zschimmer, *Chem. Ztg.*, **25**. 442, 67, 1901.

[2] E. F. Smith, *Amer. Chem. Journ.*, **4**. 279, 1883 ; *Chem. News*, **46**. 286, 1882 ; J. Volhard, *Liebig's Ann.*, **98**. 318, 1879 ; C. Bodewig, *Zeit. anal. Chem.*, **23**. 143, 1884 ; G. Carinelli, *Gazz. Chim. Ital.*, **31**. i, 544, 1901.

[3] L. C. Jones, *Zeit. anorg. Chem.*, **20**. 212, 1899 ; **21**. 169, 1899 ; A. Stock, *Compt. Rend.*, **130**. 516, 1900 ; L. Barthe, *Journ. Pharm. Chim.* (5), **29**. 163, 1894 ; J. Prescher, *Arch. Pharm.*, **242**. 194, 1904 ; P. Georgevič, *Journ. prakt. Chem.* (2), **38**. 118, 1888.

[4] R. T. Thomson (*Chem. News*, **47**. 135, 1883), after comparing litmus, methyl orange, phenolacetolin, and phenolphthalein, says : " Methyl orange is by far the best indicator for the estimation of soda in borax, and is, indeed, perfect in that respect. The change in colour at the end of the experiment is very sharply defined."

The relation between the Na_2O and the B_2O_3 in borax is not always that corresponding with $Na_2O.2B_2O_3$, because some sodium metaborate—$Na_2O.B_2O_3$—may be present. This would lead to high values when the borax is calculated from the amount of B_2O_3, since some should then have been calculated to $NaBO_2.4H_2O$.

Jacobi's Process.—Jacobi[1] abbreviates the process by taking advantage of the fact that in the presence of glycerol a solution of borax is acid to phenolphthalein, while a solution of sodium metaborate is neutral. Hence, if a solution of borax containing an excess of glycerol be titrated with ½N-sodium hydroxide, we have

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O$$

at the neutral point. After making an allowance for any acid in the glycerol, multiply the results by 0·0175, and the product represents the amount of boric oxide in the given sample; if multiplied by 0·02525, the result represents the amount of anhydrous borax; and if multiplied by 0·04775, the amount of crystalline borax.

EXAMPLE.—2 grms. of "calcined" borax were dissolved in water and mixed with glycerol and phenolphthalein. 49·65 c.c. of ½N-NaOH were needed. The glycerol added required 0·4 c.c. of the alkali for neutralisation. Hence, 49·65 − 0·4 = 49·25 c.c. were needed for the titration. Hence, the 4 grms. contained 49·25 × 0·0175 = 0·862 grm. of B_2O_3; that is, 100 × ½ × 0·862 = 43·1 per cent. boric oxide or 62·2 per cent. of "calcined" borax.

§ 304. The Evaluation of Borocalcite, Boronatrocalcite, Boracite, and Calcium Borate.

Digest, say, 10 grms. of powdered borocalcite in a flask fitted with a reflux condenser[2] (fig. 185) with, say, 50 c.c. of ½N-hydrochloric acid in order to remove the carbon dioxide, liberate the boric acid from combination, and prevent loss of boric acid by volatilisation in steam during the expulsion of the carbon dioxide. Cool. Wash the condenser tube, and the contents of the flask into a 500-c.c. standard flask with freshly boiled distilled water. The insoluble residue can be filtered off, dried, and weighed, if desired. Make the solution up to the 500-c.c. mark with water. Pipette 50 c.c. of this solution into a flask, and titrate with standard sodium hydroxide (say, ½N), using *p*-nitrophenol as indicator. When the yellow colour of the indicator appears,[3] all the hydrochloric acid has been neutralised by the soda. Note the volume of the standard sodium hydroxide required for this purpose. Pipette another 50 c.c. of the solution, add the same amount of sodium hydroxide, and then titrate with sodium hydroxide and mannitol or glycerol, with phenolphthalein as indicator, as indicated under borax and boric acid.

EXAMPLE.—10 grms. of the borocalcite were made up to 500 c.c., and 50 c.c. (*i.e.* 1 grm. of the sample) were taken for the titration. 26·6 c.c. of the soda solution were employed in the second titration. 1 c.c. of ½N-sodium hydroxide corresponds with 0·0175 grm. of boric oxide, B_2O_3. Hence, 26·6 × 0·0175 = 46·55 grm., or 46·55 per cent. B_2O_3 in the given sample.

Schaak's Process.—If appreciable quantities of iron and alumina be present, both should be separated, if possible, before the titration, since alumina will combine with the alkalies as the solution approaches the neutral point, and thus give too high a number. Schaak[1] recommends the following method of separation:—Dissolve the borocalcite as indicated above. Filter, and make the solution up to 500 c.c. Nearly neutralise 100 c.c. by titration with alkali, using methyl orange as indicator. Add 2 to 3 grms. of barium carbonate (free from alkali), warm on a steam bath for half an hour. Cool, filter, wash, and titrate the filtrate with alkali as indicated above. The first method may give values 1·5 per cent. too high, while Schaak's modification will furnish values 0·15 per cent. too high.

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[1] K. Jacobi, *Journ. Amer. Chem. Soc.*, **26**. 91, 1904.

[2] V. Kreussler, *Zeit. anal. Chem.*, **24**. 80, 1885; J. Walter, *Dingler's Journ.*, **251**. 637, 1884.

[3] Methyl orange may be used instead of the nitrophenol with satisfactory results.

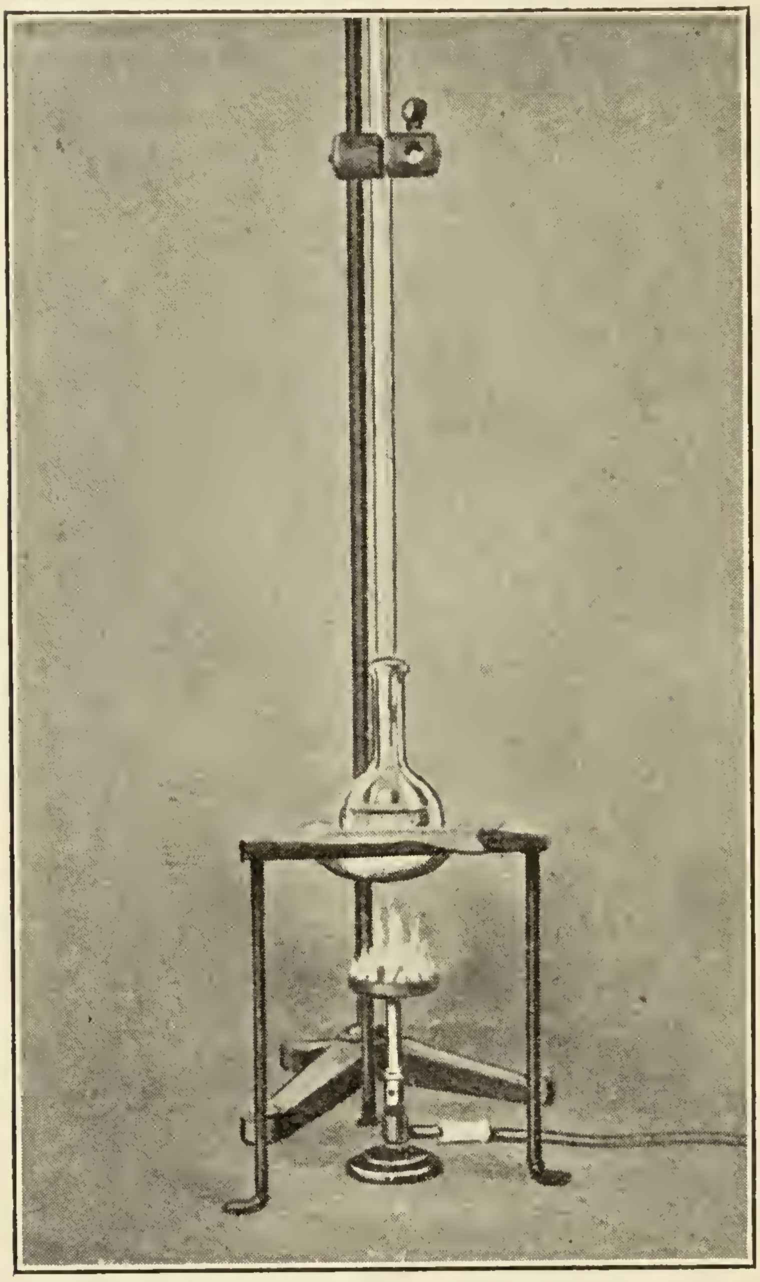

Fig. 185.—Reflux condenser (see page 303).

Jacobi's Process.[2]—The mineral borates may be rapidly evaluated by digesting, say, 2 grms. in hydrochloric acid, and evaporating the solution to dryness for silica. Add dilute hydrochloric acid, boil, filter, and wash the silica; precipitate the iron and alumina by means of ammonia; lime by ammonium oxalate; and magnesia by ammonium phosphate. Remove the excess of phosphate by means of pure ferric chloride; and remove the latter by ammonia. Evaporate the solution to dryness with concentrated nitric acid, and then twice with concentrated hydrochloric acid. Take up the residue with water, and evaporate to dryness again in a platinum dish. Heat the residue to dull redness to drive off the water and the ammonium salts. Cool, and weigh as anhydrous boric oxide, sodium (with possibly potassium) chloride, and sodium borate. Dissolve the residue in hot water, cool, and determine the soda by titration with $\frac{1}{2}$N-sulphuric acid, using methyl orange as indicator. Titrate also for total boric oxide with $\frac{1}{2}$N-sodium hydroxide, using phenolphthalein as indicator. Sum the boric oxide and the soda so obtained, and subtract the result from the weight of the residue in the platinum dish. The difference is said to be "sodium chloride," from which the Na_2O is calculated by multiplying the amount of sodium chloride by 0·5308. If potassium[3] salts and sulphates be present, their amounts are determined in separate portions. Processes like these can, of course, only give approximate results by a balancing of errors.

Lunge's Process.—In analysing boronatrocalcite, Lunge[4] dissolves the mineral in dilute hydrochloric or nitric acid, and precipitates the lime as calcium oxalate; the magnesia as phosphate. The three bases—lime, soda, and magnesia—are determined by adding a known volume of standard (hydrochloric or nitric) acid, and titrating the excess of acid with standard alkali, as indicated for borax. Deduct the results found for lime and magnesia, and the difference represents the soda.[1] Water is determined as the "loss on ignition." The difference represents the boric oxide and impurities. In one case, Kraut found 6·72 per cent. of sodium chloride and 4·74 per cent. of sodium sulphate[2] in a sample of boronatrocalcite.

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[1] M. P. Schaak, *Journ. Soc. Chem. Ind.*, 23. 699, 1904.

[2] K. Jacobi, *Journ. Amer. Chem. Soc.*, 26. 88, 1904.

[3] Or remove the boric oxide by repeated evaporation with methyl alcohol (page 589), and determine the potash and soda in the usual manner.

[4] G. Lunge, *Liebig's Ann.*, 138. 51, 1866; *Chem. News*, 15. 86, 214, 1867; K. Kraut, *Liebig's Ann.*, 139. 52, 1866. According to Lunge, there is no need to remove the boron as fluoride, since the results with and without the removal of boron "entirely coincide within the ordinary limits" of error.

§ 305. The Determination of Boric Oxide in Silicates—Wherry's Process.

Methods for the determination of boric oxide in silicates containing alumina and iron, by fusing the sample with alkali carbonate; removing the silica, alumina, etc., with ammonio-zinc oxide, Schaffgotsch's or Seeman's solutions (page 638); and finally precipitating the boric oxide as an insoluble borate—magnesium,[3] barium,[4] calcium,[5] or silver[6] borates, or potassium borofluoride,[7]—are not satisfactory, because part of the boric oxide is retained very tenaciously by the precipitated alumina. Wherry[8] recommends the following modification of Schaak's process, and it can be regarded as a good method of approximation when the time needed for the more elaborate and tedious distillation process is not available:—

Fusion.—Fuse 0·3 to 0·5 grm. of the powdered silicate with ten times its weight of sodium carbonate, and take up the cold cake with 20 to 30 c.c. of dilute hydrochloric acid. Oxidise any ferrous salts which may be present by the addition of a few drops of nitric acid or bromine water.

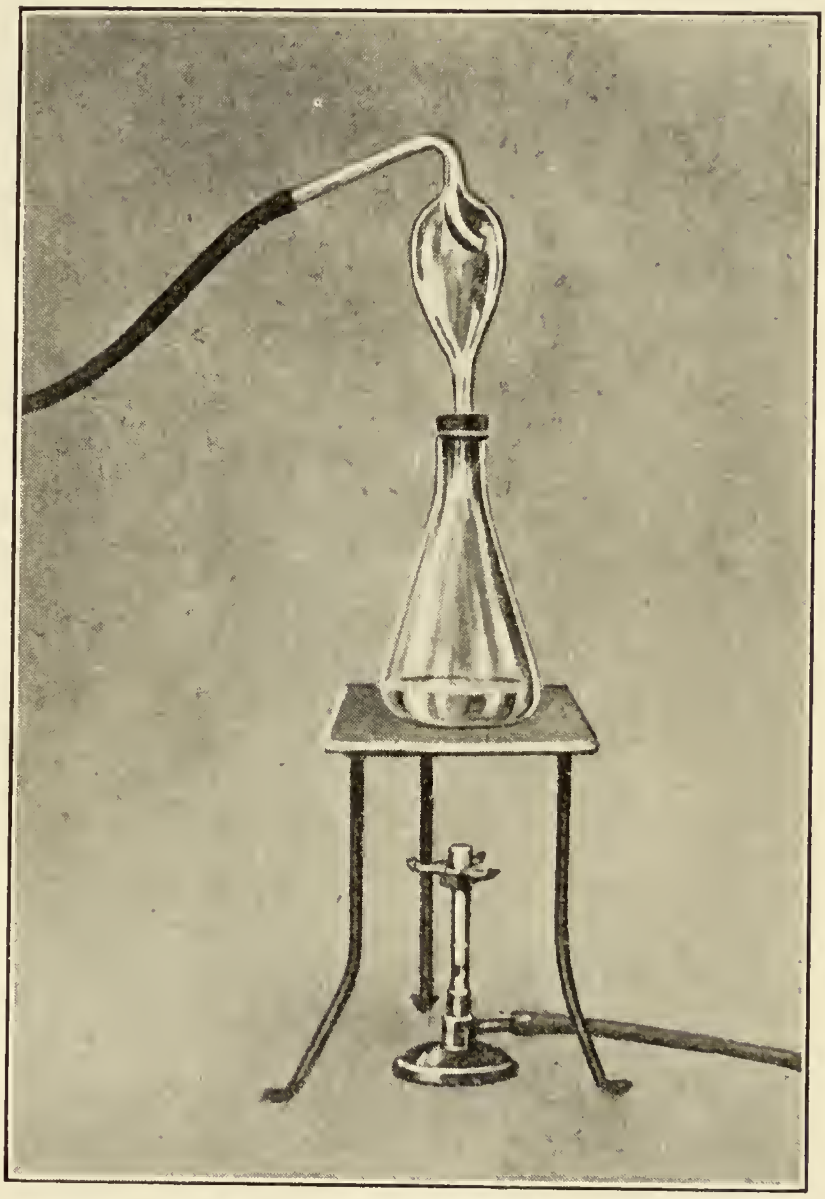

FIG. 186.—Boiling with "splash trap."

Removal of Iron and Aluminium.—Heat the mixture in a round-bottomed 250-c.c. flask nearly to boiling, and add an excess of dry precipitated calcium carbonate slowly, with constant stirring in order to precipitate the iron and aluminium hydroxides.[1] Fit a reflux condenser (figs. 128 or 185) to the flask, and boil vigorously for about 10 minutes in order to destroy bicarbonates and to expel carbon dioxide from the solution. Filter the bulky gelatinous precipitate through a Büchner's funnel (page 103) at the filter pump. Wash with hot water, but keep the volume of the liquid as low as possible—less than 100 c.c. Pour the hot filtered liquid into a 250–300 c.c. flask. Add a couple of grams of calcium carbonate. Fit a splash trap in the neck of the flask by means of a rubber stopper (fig. 186), and connect the flask with a suction pump. Heat the solution under reduced pressure for a few minutes.[2] When the liquid is cold, and boiling has ceased, filter the solution if the precipitate is red (ferric oxide); if the precipitate is white (alumina), there is no need for the filtration.

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[1] Potash is said to be rarely present.

[2] H. How, *Chem. News*, **15**. 192, 1867; F. Wöhler, *ib.*, **16**. 15, 1867.

[3] C. Marignac, *Zeit. anal. Chem.*, **1**. 405, 1862.

[4] P. von Berg, *Zeit. anal. Chem.*, **22**. 25, 1897; H. N. Morse and W. M. Burton, *Amer. Chem. Journ.*, **10**. 154, 1888.

[5] A. Ditte, *Ann. Phys. Chim.* (4), **1**. 549, 1875; *Compt. Rend.*, **80**. 490, 1875; A. Joly, *ib.*, **100**. 103, 1885.

[6] A. P. J. du Mênil, *Berzelius' Jahresber.*, **9**. 180, 1829.

[7] A. Stromeyer, *Liebig's Ann.*, **100**. 82, 1856; G. Krüss and H. Moraht, *ib.*, **260**. 180, 1896; F. Wöhler, *ib.*, **141**. 268, 1867; C. Bodewig, *Chem. News*, **50**. 49, 1884; *Zeit. anal. Chem.*, **23**. 149, 1884; C. Thaddeeff, *ib.*, **36**. 568, 1897; H. Rose, *Pogg. Ann.*, **80**. 262, 1880; C. Rammelsberg, *ib.*, **80**. 466, 1880; J. J. Berzelius, *ib*, **2**. 118, 1824.

[8] E. T. Wherry and W. H. Chapin, *Journ. Amer. Chem. Soc.*, **36**. 1687, 1908.

The Titration.—The calcium carbonate neutralises the free hydrochloric and nitric acids, but not the boric acid. Hence, the solution contains free boric acid. Titrate the solution with $\frac{1}{10}$N-sodium hydroxide. Use mannitol and phenolphthalein as indicator. If the first drop of the indicator does not strike a red colour, all the carbon dioxide has not been expelled by the boiling. In that case, acidify the solution, add an excess of calcium carbonate, and repeat the necessary operations.

Faults of the Method.—As indicated above, the weakness of this method is due to the assumption that aluminium and ferric hydroxides, precipitated by the calcium carbonate, are free from boric oxide. Some boric oxide is mechanically enclosed in the precipitate, and this can be removed by simply boiling with water; but a certain proportion of the boric oxide is so intimately associated with the hydroxides that it cannot be removed by boiling water. The boric oxide can only be recovered by redissolving the precipitate in acid, and repeating the treatment with calcium carbonate a number of times. For example, Wherry and Chapin quote these numbers:

Table LXV.—Test Analyses for Boric Oxide in Minerals.

Mineral.	Alumina or ferric oxide.	Amount used in analysis.	Per cent. boric oxide.					
			First.	Second.	Third.	Fourth.	Fifth.	Total.
	Per cent.	Grm.						
Dumortiertite . .	63	0·5	3·87	1·12	0·35	0·11	...	5·45
Ludwigite . . .	40	0·3	9·93	0·71	0·71	0·52	0·22	12·09
Danburite . . .	nil.	0·3	23·77	0·29	...	...	...	24·06
Tourmaline . . .	35	0·3	8·88	0·82	0·23	...	...	9·93
Vesuvianite . . .	20	0·3	1·75	0·17	...	...	...	1·92

The results are in general better with small proportions of boric oxide, as we should expect. The process can therefore only be recommended when an approximate determination is needed. If results are desired with any pretence to accuracy, the distillation process must be employed. The necessary repetition of the processes of solution and precipitation, as indicated above, makes the distillation process less troublesome and more reliable than the calcium carbonate precipitation process.

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[1] It is impossible to prevent the precipitation of some boric oxide with the iron and aluminium hydroxides.

[2] If the exhaustion is conducted too rapidly, violent frothing and loss of material may render it necessary to start the analysis again.

§ 306. The Determination of Boric Oxide in Silicates—Distillation Process.

If methyl alcohol be distilled from a mixture containing free boric acid, methyl borate, boiling at 65°, distils over. The methyl borate can be saponified with alkalies, etc., and the boric acid determined by gravimetric or volumetric processes. This reaction was simultaneously employed by Gooch and by Rosenbladt in 1887, and it has since been extensively used[1] for the determination of boric oxide in silicates and alumino-silicates. Ethyl alcohol can be employed,[2] but it forms ethyl borate, boiling at about 120°. In consequence of the higher boiling point of ethyl borate, methyl alcohol,[3] though more expensive, is more effective than ethyl alcohol.

Preparation of the Sample for Distillation.—Fuse 0·5 grm.[4] of the sample with 6 grms. of sodium carbonate (page 164). When the crucible is cold, the cake[5] is transferred to a 250-c.c. flask by using 50 c.c. of water and 5 c.c. of concentrated hydrochloric acid for the purpose. This amount of acid is sufficient to neutralise the sodium carbonate used in the fusion. The flask is then fitted with a reflux condenser (fig. 185), and boiled for an hour in order to drive off the carbon dioxide. The reflux condenser is to prevent loss due to volatilisation of boric acid with the issuing steam. *Aqueous solutions of boric acid must never be boiled in open vessels when the boric acid is to be determined quantitatively.*[6] Wash the condenser tube with a little water and collect the runnings in the flask. Now add solid granular anhydrous calcium chloride to the flask. About 1 grm. of the salt per c.c. of liquid will suffice. Rotate the flask for a few minutes in order to ensure a thorough mixing of the contents. In adding the calcium chloride, keep the neck of the flask clean. The object of the calcium chloride is to prevent the hydrolysis of the methyl borate in the flask, and thus facilitate its removal. Sulphuric or phosphoric acid can also be employed as dehydrating agent.[1]

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[1] K. Farnsteiner, *Zeit. Nahr. Genuss.*, **3**. 1, 1900; K. Windisch, *ib.*, **9**. 641, 1905; R. Fischer, *ib.*, **3**. 17, 1900; J. Wolff, *ib.*, **3**. 600, 1900; **4**. 157, 1901; J. J. Ebelmen and Bouquet, *Ann. Chim. Phys.* (3), **17**. 54, 1846; J. J. Ebelmen, *ib.* (3), **16**. 129, 1846; H. Schiff, *Liebig's Ann.*, *Suppl.*, **5**. 154, 1867; H. Schiff and E. Bechi, *Compt. Rend.*, **61**. 697, 1865; H. Copaux, *ib.*, **127**. 756, 1888; H. Moissan, *ib.*, **156**. 1084, 1893; S. L. Penfeld and E. S. Sperry, *Amer. J. Science* (3), **34**. 222, 1887; J. E. Whitfield, *ib.* (3), **34**. 281, 1887; C. E. Cassal, *Analyst*, **15**. 230, 1890; A. K. Reischle, *Zeit. anorg. Chem.*, **4**. 111, 1893; A. Mandelbaum, *ib.*, **62**. 364, 1909; K. Kraut, *Zeit. anal. Chem.*, **36**. 165, 1897; A. W. Blyth, *Proc. Chem. Soc.*, **15**. 51, 1899; C. Montemartini, *Gazz. Chim. Ital.*, **28**. i. 344, 1898; G. H. Beermann, *Kritische Studien über die neueren quantitativen Bestimmungsmethoden der Borsäure mit Einschluss der Turmalinanalyse*, Berlin, 1898; J. Prescher, *Arch. Pharm.*, **242**. 194, 1904; A. Schneider and Gaab, *Pharm. Centr.*, **37**. 372, 1896; W. H. Low, *Chem. News*, **95**. 52, 61, 73, 1907; *Journ. Amer. Chem. Soc.*, **28**. 807, 1907; E. T. Wherry and W. H. Chapin, *ib.*, **30**. 1687, 1908; G. W. Sargent, *ib.*, **21**. 858, 1899; L. de Koningh, *ib.*, **19**. 55, 1897; O. von Spindler, *Schweizer Wochenschrift Chem. Pharm.*, **43**. 659, 1906; *Chem. Ztg.*, **29**. 566, 1905; R. Arndt, *ib.*, **33**. 725, 1909; H. Copaux and G. Boiteau, *Bull. Soc. Chim.* (4), **5**. 217, 1909 (the distillation process will not do with boric oxide in the presence of tungstates); G. Bertrand and H. Agulhon, *ib.* (4), **7**. 125, 1910; H. Fromme, *Tschermak's Mitt.*, **28**. 329, 1910; E. Polenske, *Arbeit. Kaiser. Gesund.*, **17**. 564, 1900; **19**. 167, 1909; A. Gunther, *ib.*, **19**. 489, 1904; G. Raulin, *Monit. Scient.* (5), **1**. 434, 1911.

[2] H. Rose, *Pogg. Ann.*, **80**. 262, 1846.

[3] Avoid the use of methyl alcohol, which blackens or evolves sulphur dioxide when heated with sulphuric acid on a water bath.

[4] For substances containing a high proportion of boric oxide, 0·25 grm. may be used. The total boric oxide should be kept below 0·1 grm., otherwise the distillation will require a long time, the titration will require a large volume of solution, and the end point will be less distinct. If metals likely to injure the platinum crucible are present, the substance may be fused in a porcelain crucible (felspathic glaze), and the crucible and cake powdered and treated as described in the text.

[5] The first residue from the Smith's process for alkalies may be dried and then used for this determination.

[6] Note the violation of this rule in Jacobi's process for mineral borates (page 582).

The Distillation Apparatus.—An apparatus similar to that indicated in fig. 188 is to be fitted up. *A* is a 250-c.c. distilling flask[2] containing the boric acid, etc., prepared as indicated above. *B* is a 500- to 800-c.c. distilling flask containing methyl alcohol free from acetone. Owing to violent bumping which occurs when methyl alcohol is boiled in glass vessels, a boiling tube[3] is necessary

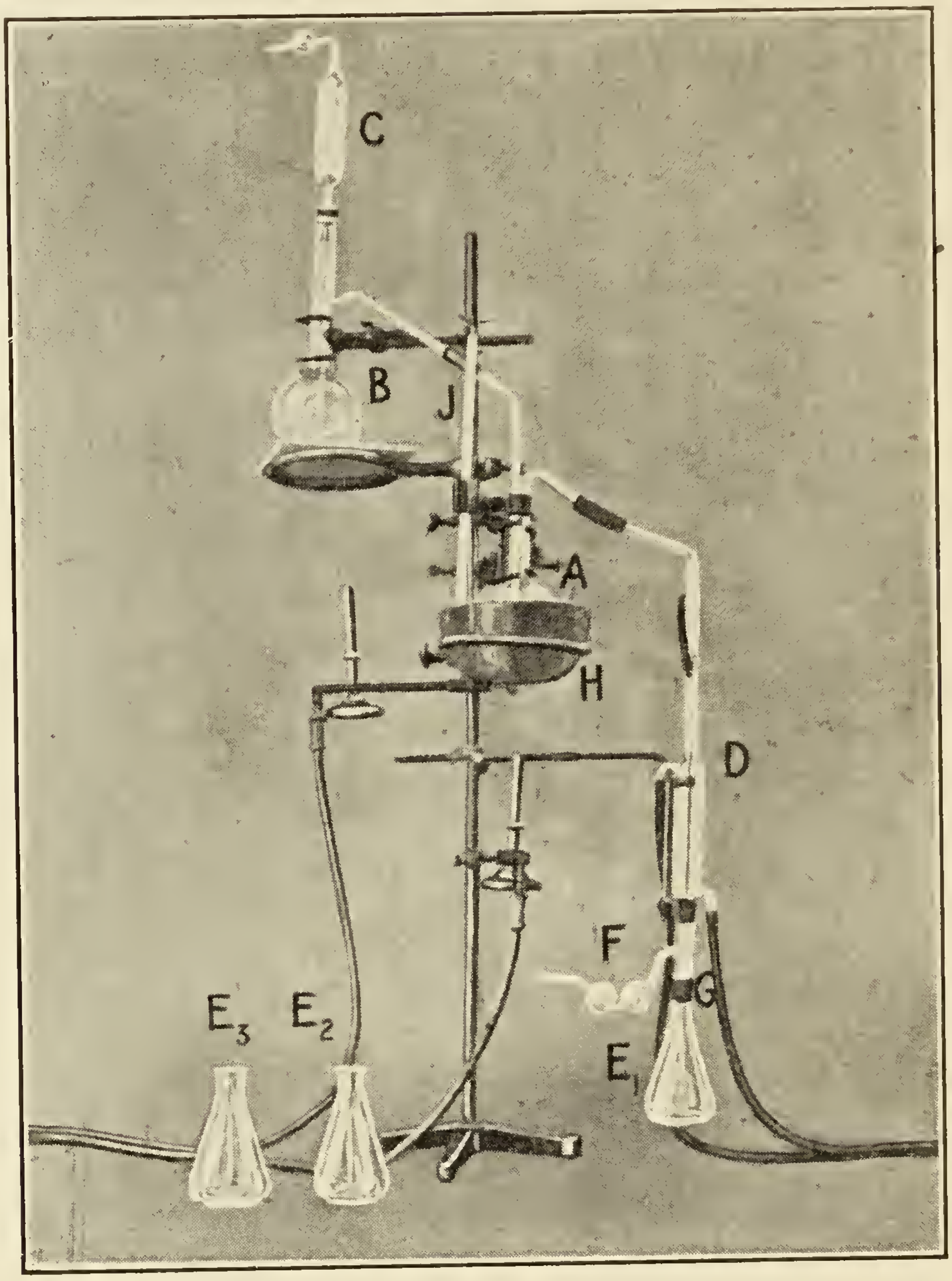

Fig. 187.—Distillation apparatus.

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[1] If strong acids be used for the distillation, and if chlorides be present, chlorine may be evolved. In that case, it is well to remove the chlorine by precipitation with silver nitrate and proceed with the distillation at once. The silver nitrate, if desired, can be removed by precipitation with sodium hydroxide or carbonate. Similar remarks apply to the presence of nitrates, oxalates, citrates, tartrates (but not acetates) when the distillation is made from concentrated sulphuric acid in place of the calcium chloride indicated in the text. For Rosenbladt's suggestion to use silver sulphate in the flask, see page 547.

[2] Bohemian glass should be used. Some varieties of glass contain boric oxide, and are consequently a source of danger. A Lewkowitsch's flask (J. Lewkowitsch, *Journ. Chem. Soc.*, 55. 360, 1889 ; G. George, *Chem. News*, 78. 259, 1898) with a wide delivery tube may be used.

[3] Boiling Tubes.—This important auxiliary is a simple and effective means of preventing the bumping of most liquids during boiling, and it has the advantage of introducing no other foreign substance than glass and air. It would be almost impossible to conduct experiments with boiling methyl alcohol if some device of this character were not employed. The boiling tube here described appears to have been first suggested by D. Gernez (*Compt. Rend.*, 86. 472, 1878 ; H. Scudder, *Journ. Amer. Chem. Soc.*, 25. 163, 1903 ; *Chem. News*, 88. 242, 1903).

each time the flask is used. *C* is a small Fresenius' gas washer[1] containing a little mercury. This acts as a safety valve should the tube leading from *B* to *A* get clogged. *C* can be fitted with a long exit tube to carry the vapours of alcohol away from the proximity of the flame should alcohol blow out. *D* is a Lendrich's condenser.[2] *E* is a 250-c.c. Erlenmeyer's flask to act as a receiver. It is fitted with a tube *F* containing enough water to act as a water seal and prevent the loss of methyl borate during the distillation. From four to six condensing flasks, *E*, are used, and all fit on the same stopper, *G*. The connections are made as indicated in the diagram.

The Distillation.—The flask *B* is heated, and methyl alcohol vapour distils into the flask *A*. When about 25 c.c. of alcohol have condensed in *A*, the latter flask is heated[3] hot enough to prevent any further condensation of alcohol vapour in *A*. The distillation must not proceed too rapidly, or methyl borate may be lost through the water trap. When about 100 c.c. of alcohol have condensed, change the receiver. Transfer the contents of the trap *F* to the flask just removed. Add a drop of *p*-nitrophenol to the same flask, and run in the standard soda solution until the free acid is neutralised. To titrate for boric acid, add 1 c.c. of phenolphthalein, and titrate until the pink coloration has developed. The end reaction is not very sharp, owing to the action of the alcohol on the indicator. The difference between the burette readings with the two indicators gives an approximation to the amount of boric acid in the distillate. Add to the distillate twice as much standard alkali as was required in the phenolphthalein titration for boric acid. If 5 c.c. of alkali were required for the boric acid titration, add 10 c.c. of the same alkali. The object of adding the excess of alkali is to prevent loss of boric acid[4] when the alcohol is distilled off later on. When another 100 c.c. has collected in the second Erlenmeyer flask, change the receiver, and treat the distillate as before. If less

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It is made as follows:—Draw out a piece of glass tubing until its internal bore is from 0·5 to 1·0 mm. diameter. The tube is sealed (*c*, fig. 188) about 1 cm. from one end, *a*, by holding

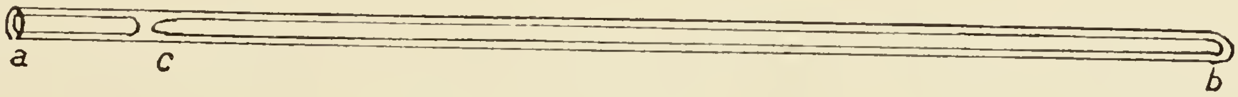

FIG. 188.—Boiling tube.

the tube in the flame until the sides have run together. Cut the tube the desired length—say, 16 cm.—and seal the end *b* to prevent the entrance of liquid. The upper end of the boiling tube should reach very nearly to the top of the flask. The tube is placed open end down in the liquid. The open end *a* should rest on the bottom near the hottest part of the flask, and remain there during the boiling. Hence, the tube should be heavy enough to prevent its being thrown off the bottom. For liquids of high specific gravity, therefore, it may be necessary to use a piece of thick-walled capillary tubing with a wide bore (may be up to 5 mm.); and for frothing liquids, and liquids of low boiling point, a narrow boiling tube is best.

The action of the boiling tube is as follows:—The air in *ac* expands and passes through the liquid in small bubbles. The air is gradually replaced by the vapour of the liquid being boiled, and the stream of bubbles is continuous so long as the temperature about the capillary is at the boiling point of the liquid. This prevents superheating and explosive boiling. The seal *c* should be below the surface of the liquid, even if it be necessary to bend the portion *ab* for the purpose and make *ac* nearly parallel with the bottom of the flask. This prevents the condensation of vapour in *ac*, which would stop the stream of bubbles. The flame should be protected from draughts so as to prevent the temperature of the liquid falling below its boiling point and thus causing the capillary to fill with liquid. The boiling tube is useless if it be filled with liquid. Hence it should be cold and empty when placed in the flask. The liquid is shaken out of the boiling tube each time it is used.

[1] R. Fresenius, *Zeit. anal. Chem.*, 15. 62, 1876.

[2] K. Lendrich, *D.R.G.M.* 198543, 1903; F. Allihn, *Zeit. anal. Chem.*, 25. 36, 1886.

[3] In a paraffin bath *H*; the thermometer *J* shows the temperature of the paraffin bath.

[4] According to E. Polenske (*Arbeit. Kaiser. Gesund.*, 17. 564, 1900), a mixture of soda and boric acid corresponding with $5Na_2O.4B_2O_3$ is stable in boiling methyl alcohol.

than 1 c.c. $\frac{1}{10}$N-sodium hydroxide be required, or 0·2 c.c. of $\frac{1}{2}$N-sodium hydroxide be required for the boric acid titration, the distillation is completed. If more than this amount of alkali be required, continue the distillation, a third, and may be a fourth time. If sufficient calcium chloride has been used, the second distillation is usually sufficient.[1]

The following readings were made during a determination of the boric oxide in 0·5 grm. of glaze :—

Indicator ($\frac{1}{2}$N-NaOH).	First distillate.	Second distillate.	Third distillate.	Total.
p-Nitrophenol	2·7	0·3	0·2	3·2
Phenolphthalein . . .	4·1	0·4	0·1	4·6

Hence, in all, 4·6 c.c. of the $\frac{1}{2}$N-NaOH solution were used for the H_3BO_3 in the phenolphthalein titration. Add 9·2 c.c. of the $\frac{1}{2}$N-NaOH in order to fix the boric acid during the next stage of the operation.

Removal of Methyl Alcohol from the Distillate.—The distillates are now poured into a flask. Use as little water as possible for the rinsing. A boiling tube is placed in the flask, and the flask is heated. The alcohol which distils off is collected in a receiver placed below the condenser.[2] When the alcohol has distilled off, change the receiver. The residue should occupy about 25 c.c. If less, make up to approximately this volume with distilled water. Add concentrated hydrochloric acid (1 : 1) drop by drop until the colour of the indicator is just discharged. Put a boiling tube into the flask, and heat the solution on the steam bath for about two minutes. The flask is then connected with the filter pump and the liquid allowed to cool while the pump is in action. This decomposes any carbonates, and there is no danger of losing boric oxide. The liquid should be colourless hot or cold. If otherwise, sufficient acid is not present.

Final Titration of the Boric Oxide.—Neutralise any excess of acid with $\frac{1}{2}$N-sodium hydroxide until the yellow tint of the nitrophenol appears. Make the solution acid with $\frac{1}{10}$N-hydrochloric acid, and again neutralise with the $\frac{1}{10}$N-alkali. One drop of the $\frac{1}{10}$N-acid should discharge the colour of the indicator. Now add 1 grm. mannitol (or 40 c.c. of glycerol) and titrate with $\frac{1}{10}$N- or $\frac{1}{2}$N-alkali according to the amount of boric oxide present (the methyl alcohol titration shows this), as indicated under boric acid.

With the sample previously discussed, the following readings were made :—23·6 c.c. of $\frac{1}{10}$N-NaOH were required. 1 c.c. of the $\frac{1}{10}$N-NaOH corresponded with 0·003322 grm. B_2O_3.[3] Hence, $23·6 \times 0·003322 = 0·07835$ grm. B_2O_3 was present per 0·5 grm. of the glaze; or the glaze contained 15·67 per cent. of boric oxide—B_2O_3.

Test Experiments.—Determinations with artificial mixtures of known amounts of boric oxide with sodium silicate; alum; potassium fluoride; ferric and ferrous salts; arsenious, zinc, stannous, and antimonious salts; salts of the alkalies and alkaline earths gave quite satisfactory results. 0·0350 grm. of boric oxide was used in the following determination with three different mixtures of the substances just enumerated :

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[1] Instead of passing the vapour of methyl alcohol through the boric acid solution, flasks *B* and *C* may be dispensed with, and a stoppered separating funnel fixed in *A*—as in the original Gooch's apparatus. Then add liquid methyl alcohol in separate portions 10 c.c. at a time. Six additions then usually suffice (G. W. Sargent, *Journ. Amer. Chem. Soc.*, 21. 858, 1899).

[2] The alcohol may be recovered by distillation from quicklime and 100 c.c. of a concentrated solution of caustic soda. The distillate should give no reaction for boric acid.

[3] The $\frac{1}{10}$N-NaOH was standardised against boric acid.

First distillate (100 c.c.) required .	2·2	1·9	1·9	c c. $\frac{1}{2}$N-NaOH.
Second distillate (100 c.c) required .	0·4	0·5[1]	0·3	c.c. $\frac{1}{2}$N-NaOH.
Total B_2O_3 found	0·0348	0·0346	0·0352	grm.

Hence, it is inferred that the substances above enumerated did not interfere with the volatilisation of the boric oxide, nor with its accurate titration afterwards.

Other Methods of collecting the Methyl Borate.—Instead of decomposing the distillate with sodium hydroxide as indicated above, Thaddeeff[2] collected the distillate in a solution of caustic potash, and subsequently precipitated the boric acid as potassium borofluoride; Rosenbladt[3] hydrolysed the methyl borate with magnesia; Gooch[4] used calcium oxide for the same purpose. In the two latter cases the contents of the distilling flask were acidified with nitric or acetic acid (Gooch), or a non-volatile acid—sulphuric (Rosenbladt) or phosphoric (Gladding)[5] acid. The magnesia, being insoluble, does not act very rapidly, and lime is difficult to calcine to a constant weight on account of its tendency to absorb carbon dioxide and moisture. Hehner used disodium phosphate;[6] Schneider and Gaab,[7] sodium carbonate; Stolba,[8] borax; and Gooch and Jones,[9] sodium tungstate (approximately 5 grms. per 0·1 grm. B_2O_3). The last-named substance has the advantage of being easily obtained pure, and it is soluble in water, so that the hydrolysis proceeds comparatively quickly.[10]

§ 307. Determination of Silica and Alumina in Boro-silicates.

In the analysis of silicates containing boric oxide, only part of the boric oxide is lost during the two evaporations to dryness; the other part of the boric oxide is precipitated with the alumina and iron. This furnishes high results.[11] To eliminate the boric oxide in the silica evaporations, add methyl alcohol, or better (Jannasch)[12] methyl alcohol[13] saturated with hydrogen chloride, to the basin in which the evaporation for silica is being conducted. If the first "silica filtrate" gives an indication of boric oxide, the treatment may be repeated with the second "silica evaporation."

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[1] A third distillate (100 c.c.) contained the equivalent of 0·0005 grm. B_2O_3.

[2] C. Thaddeeff, *Zeit. anal. Chem.*, **36.** 568, 1897.

[3] T. Rosenbladt, *Zeit. anal. Chem.*, **26.** 1887 ; *Chem. News*, **55.** 18, 101, 1887.

[4] F. A. Gooch, *Amer. Chem. Journ.*, **9.** 23, 1887 ; *Chem. News*, **55.** 7, 1887 ; C. Marignac, *Zeit. anal. Chem.*, **1.** 406, 1862 ; K. Kraut, *ib.*, **36.** 165, 1897 ; S. L. Penfield and E. S. Sperry, *Amer. J. Science* (3), **34.** 220, 1887. A gram of lime, for instance, is weighed and evaporated to dryness with the methyl borate after ignition. The increase in weight represents boric oxide. The solid "crawls" badly during the evaporation, and the methyl alcohol "bumps" badly if it is allowed to boil.

[5] T. S. Gladding, *Journ. Amer. Chem. Soc.*, **20.** 258, 1898 ; M. P. Schaak, *Journ. Soc. Chem. Ind.*, **23.** 699, 1904 ; H. Lührig, *Pharm. Centr.*, **42.** 50, 1901. C. Fresenius and O. Popp (*Zeit. öffent. Chem.*, **3.** 155, 188, 1897) used anhydrous sodium sulphate.

[6] O. Hehner, *Analyst*, **16.** 141, 1891.

[7] A. Schneider and Gaab, *Pharm. Centr.*, **7.** 672, 1897.

[8] F. Stolba, *Journ. prakt. Chem.* (2), **90.** 457, 1863 ; R. J. Manning and W. R. Lang (*Journ. Soc. Chem. Ind.*, **26.** 803, 1907) precipitate the boric oxide by barium chloride in the distillate and weigh as $Ba(BO_2)_2$.

[9] F. A. Gooch and L. C. Jones, *Amer. J. Science* (4), **7.** 34, 1899 ; *Chem. News*, **79.** 99, 111, 1899.

[10] The sodium tungstate, freed from carbonate by fusion with a little tungstic acid, is weighed in a platinum dish and then placed in the Erlenmeyer's flask *F* (fig. 188). After the distillation, methyl alcohol is boiled off, and the contents are transferred to the same platinum dish as was used for weighing the sodium tungstate. Evaporate to dryness, fuse as before, cool, and weigh. The increase in weight represents the boric oxide.

[11] F. Wöhler, *Liebig's Ann.*, **141.** 268, 1867 ; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **28.** 324, 1889 ; W. Hampe, *Chem. Ztg.*, **15.** 521, 1891.

[12] P. Jannasch, *Zeit. anorg. Chem.*, **12.** 208, 1896 ; *Zeit. anal. Chem.*, **36.** 383, 1897.

[13] The methyl alcohol should not blacken or evolve sulphur dioxide when heated with sulphuric acid on a water bath.

CHAPTER XLI.

THE DETERMINATION OF PHOSPHORUS.

> An accurate determination of phosphoric oxide, by whatever method it is made, requires much skill and not a little practice. The advocate of one method often makes the other suffer in comparison, more by reason of his own want of skill in the manipulation of the method than by reason of any great advantage inherent in his own.—A. A. BLAIR.[1]

§ 308. The Properties of Ammonium Phosphomolybdate.

THE methods for the determination of phosphorus have probably been the subject of more investigations than any other analytical process. The subject, though clarified a little, is by no means definitely settled, since a number of contradictory statements confront the student of the subject. These can only be decided in the laboratory, but the very fact that the phenomena connected with this determination have led to a number of contradictions is a remarkable testimony to the obscurity of the reactions involved. In the valuation of phosphates by chemists selected by buyer and by seller, I have been informed that differences involving 10–15 per cent. of the total cost of the materials were at one time by no means uncommon; and many analytical chemists were accordingly classed by sellers and buyers as "high" and "low" analysts.[2] The buyer naturally favoured the "low" analyst; the seller, the "high" analyst. The differences, in most cases, were probably due to the need for standard methods of analysis, particularly in dealing with so imperfect and faulty a method of analysis as was then in vogue.

In 1851, Sonneschein showed that the reaction between ammonium molybdate and orthophosphoric acid, discovered by Svanberg and Struve[3] three years earlier, could be employed for the quantitative determination of phosphorus. The precipitation of the orthophosphoric acid[4] takes place in the presence of iron, aluminium, lime, magnesia, and the alkalies.

The yellow ammonium phosphomolybdate is but sparingly soluble in water. According to Chesneau,[5] 0·030 grm. of the ammonium phosphomolybdate dissolves in a litre of water at 15°. This means that if a litre of water comes in contact with the precipitate, 0·030 grm. will pass into solution.

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[1] A. A. Blair, *Chem. News*, **56**. 246, 1887.

[2] A. E. Davies, *Chem. News*, **23**. 220, 1871.

[3] L. Svanberg and H. Struve, *Journ. prakt. Chem.* (1), **44**. 257, 1848; H. Struve, *ib.* (1), **54**. 288, 1851; L. Sonneschein, *ib.* (1), **53**. 339, 1851; H. Rose, *Pogg. Ann.*, **76**. 26, 1849.

[4] If meta- or pyro-phosphoric acids be present, they ought to be oxidised—with, say, potassium permanganate or chromic acid. If a brown precipitate of manganese peroxide be produced, insoluble in acids, a small quantity of potassium nitrite will clear the solution. The manganese dioxide is reduced to MnO, which dissolves in the acid. Nitric acid and potassium chlorate are not always vigorous enough to convert the meta- and pyro- to ortho-phosphoric acid. C. Meineke and E. F. Wood, *Rev. Univ. Mines* (3), **9**. 235, 1890; M. von Reiss, *Stahl Eisen*, **9**. 1025, 1889; **10**. 1059, 1890.

[5] C. Chesneau, *Rev. Met.*, **5**. 237, 1908; V. Eggertz, *Journ. prakt. Chem.* (1), **79**. 496, 1860; F. Hundeshagen, *Chem. News*, **60**. 169, 177, 188, 201, 205, 1889; *Zeit. anal. Chem.*, **28**. 164, 1889; **32**. 144, 1893; R. Fresenius, *ib.*, **3**. 446, 1864; G. Jorgensen, *ib.*, **45**. 273, 1906;

Action of Nitric Acid.—Hundeshagen represents the reaction between ammonium molybdate and, say, sodium phosphate by the equation :

$$Na_3PO_4 + 12(NH_4)_2MoO_4 + 26HNO_3 = (NH_4)_3PO_4 . 12MoO_3 . 2HNO_3 . H_2O + \text{etc.},$$

where 1 grm. of phosphoric anhydride—P_2O_5—corresponds with 23 grms. of nitric acid—HNO_3. But the amount of nitric acid can be increased considerably beyond this limit without interfering with the precipitation. If, however, the quantity of the nitric acid rises above 71 grms. HNO_3 per gram of P_2O_5, the precipitate of ammonium phosphomolybdate will be partially decomposed, and the precipitation will consequently be incomplete. If over 1700 grms. of HNO_3 per gram of P_2O_5 be present, no ammonium phosphomolybdate will be precipitated. Both hydrochloric and sulphuric acids act more powerfully than nitric acid. In consequence, *nitric acid gives the widest margin of safety between a sufficient quantity and an overdose of acid.* The solvent effects of an overdose of nitric acid can be overcome by adding an excess of molybdate. The greater the excess of acid, the greater the amount of molybdate required for the complete precipitation of the phosphate. Chesneau gives the solubility of ammonium phosphomolybdate in dilute nitric acid as follows :

Table LXVI.—Solubility of Ammonium Phosphomolybdate in Nitric Acid.

Nitric acid.	Ammonium phosphomolybdate dissolved per 100 c.c. acid.
Per cent.	Grm. at 15°.
0	0·0030
1	0·0371
5	0·0682
10	0·0901

This table shows that nitric acid augments the solubility of the precipitated ammonium phosphomolybdate.

Action of Ammonium Nitrate.—Chesneau gives the solubility of ammonium phosphomolybdate in aqueous solutions of ammonium nitrate as follows :

Table LXVII.—Solubility of Ammonium Phosphomolybdate in Aqueous Solutions of Ammonium Nitrate.

Ammonium nitrate.	Ammonium phosphomolybdate dissolved per 100 c.c. solution.
Per cent.	Grm. at 15°.
0	0·0030
5	0·0099
10	0·0113

Analyst, **34**. 372, 1909 ; *Mem. Acad. Roy. Soc. Danemark* (7), **2**. 141, 1905 ; *Zeit. angew. Chem.*, **24**. 542, 1911 ; R. Finkener, *Ber.*, **11**. 1638, 1878. Some say that the solubility of the precipitate is decreased, and some say that the solubility is increased, by the addition of ammonium nitrate.

This shows an increase in the solubility of ammonium phosphomolybdate in the presence of ammonium nitrate. In the absence of ammonium nitrate, the precipitate is inclined to separate in a colloidal condition which is exceedingly difficult to filter clear. Hundeshagen showed that this will occur if less than 0·5 per cent. of ammonium nitrate be present in the solution. The precipitate, even when this amount is present, settles slowly. In order to get rapidly settling precipitates, from 5 to 15 per cent. of ammonium nitrate should be present in the solution. Besides accelerating the rate of settling, ammonium nitrate also accelerates the rate of precipitation, and ensures a more complete precipitation with a smaller excess of ammonium molybdate.[1] These facts are illustrated by the following numbers. The conditions in the different experiments were otherwise the same.

Table LXVIII.—Effect of Ammonium Nitrate on the Precipitation of Ammonium Phosphomolybdate.

Ammonium molybdate.	Amount of P_2O_5 precipitated.	
	No nitrate.	10 grms. of nitrate.
c.c.		
50	0·1100	0·1165
60	0·1156	0·1160
70	0·1155	0·1160
80	0·1158	0·1162
90	0·1165	0·1163

Hence, 50 c.c. of a given solution of ammonium molybdate will precipitate all the phosphoric acid in a given solution in the presence of ammonium nitrate, under conditions where 5·6 per cent. may escape precipitation in the absence of the ammonium nitrate.

Influence of Temperature.—The precipitate forms rather more quickly in hot solutions. According to Hundeshagen, if the ammonium phosphomolybdate be precipitated in the cold, it separates in the form of rounded grains of different sizes, which settle very slowly. Such precipitates are inclined to choke the pores of the filter paper and retard filtration. If the precipitation occurs in hot solutions, the ammonium phosphomolybdate separates in the form of octahedral crystals (usually grouped "rosettenförmig"), which settle rapidly and filter easily. The precipitate formed in hot solutions is also easier to wash. If the temperature of the solution be above 60°, white needles of ammonium tetramolybdate may be produced by a prolonged heating, and this the more, the higher the temperature, and the longer the solution is heated. Ammonium tetramolybdate is soluble in water and nitric acid, but is precipitated by ammonium nitrate. When ammonium tetramolybdate is once formed, it will contaminate the precipitate even if the ammonium phosphomolybdate be dissolved and reprecipitated a second time. Hence, in order to avoid this source of error,[2] the solution should not be heated too long a time, nor at too high a temperature.

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[1] E. Richters, *Zeit. anal. Chem.*, **10.** 471, 1871 ; E. Stunkel, T. Wetzke, and P. Wagner, *ib.*, **21.** 353, 1882 ; F. Hundeshagen, *ib.*, **28.** 141, 1889 ; C. Gilbert, *Correspondenz Ver. anal. Chem.*, 1, 1878.

[2] In illustration of the different ideas which prevail as to the time and temperature of heating required for complete precipitation, the following may be quoted :—R. Fresenius (*Zeit.

Composition of the Precipitate.—The actual composition of the precipitate depends upon the time of standing, temperature, and the nature of the mother liquid. This partly explains how so many different factors have been proposed for converting the weight of the precipitate into the equivalent "P_2O_5." Thus, factors varying from 3·03 per cent. P_2O_5 (Sonneschein) to 4·39 per cent. (Debray) have been suggested. The following selection[1] will illustrate the different results which have been obtained for the composition of the yellow ammonium phosphomolybdate:

	Rammelsberg.	Sonneschein.	Gibbs.	Gladding.
H_2O	5·77	11·23	3·94	2·44
NH_4 . . .	3·25	11·23	3·35	2·44
P_2O_5 . . .	3·90	3·03	3·66	3·76
MoO_3 . . .	86·45	86·87	89·05	91·36

Indeed, if the precipitation be not performed under definite conditions, there is some uncertainty as to the composition of the precipitate. Hence, the precipitate is frequently redissolved in ammonia and reprecipitated in the form of ammonium magnesium phosphate, or as ammonium phosphomolybdate.

Chesneau[2] has studied this phase of the subject. He found that when ammonium nitrate is absent, the precipitate weighs less than theory requires, and this the more with solutions containing small amounts of phosphorus. When ammonium nitrate is present, the precipitate with solutions poor in phosphorus is heavier than theory requires. As a matter of fact, the precipitate is not always a single compound, but a mixture of different substances—ammonium phosphomolybdate, molybdic acid, ammonium tetramolybdate, and occluded ammonium molybdate.[3] When ammonium nitrate is absent, the amount of molybdic acid in the precipitate increases with increasing concentration of the phosphoric acid, up to a certain definite limit. When ammonium nitrate is present, the amount of molybdic acid increases as the amount of phosphorus decreases. When no molybdic acid crystals are present, as will be the case when about 0·005 grm. of phosphorus is present, the stellate crystals of ammonium phosphomolybdate predominate. If the amount of phosphorus be reduced to 0·00027 grm., the precipitate will be contaminated with prismatic crystals of ammonium tetramolybdate.

Influence of Ammonium Salts.—Fresenius[4] has shown that the presence of

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anal. Chem., **3.** 446, 1864)—6 hrs. at 65° ; R. Fresenius (*Anleitung zur quantitative chemischen Analyse*, Braunschweig, **1.** 411, 1875)—12 hrs. at 40° ; O. Abesser, W. Jani, and M. Märcker (*Zeit. anal. Chem.*, **12.** 254, 1873)—4 to 6 hrs. at 50°; C. Stünkel, T. Wetzke, and P. Wagner (*ib.*, **21.** 353, 1882)—1 hr. at 80° to 90°. P. Pietsch, W. Rohn, and P. Wagner, *Zeit. anal. Chem.*, **19.** 444, 1880 ; R. de Roode, *Journ. Amer. Chem. Soc.*, **17.** 43, 1895 ; M. Fleischer and K. Müller, *Journ. Landw.*, **20.** 96, 1875.

[1] C. Rammelsberg, *Ber. Berl. Akad.*, 573, 1877 ; *Ber.*, **10.** 1776, 1877 ; R. Finkener, *ib.*, **11.** 1638, 1878 ; L. Sonneschein, *Journ. prakt. Chem.* (1), **53.** 339, 1851 ; M. Seligsohn (1), **67.** 470, 1856 ; V. Eggertz, *ib.* (1), **79.** 490, 1860 ; W. Gibbs, *Amer. Chem. Journ.*, **3.** 317, 406, 1881 ; *Proc. Amer. Acad.*, **18.** 232, 1883 ; **21.** 96, 1885 ; *Chem. News*, **45.** 29, 1882 ; H. Debray, *ib.*, **17.** 183, 1868 ; *Compt. Rend.*, **66.** 702, 1868 ; D. J. Hissink and H. van der Waerden, *Chem. Weekblad*, **2.** 179, 1905 ; G. A. Spiess, *Viertelj. Pharm.*, **9.** 257, 1860 ; M. Nutzinger, *ib.*, **4.** 549, 1855 ; J. König, *Landw. Ver. Stat.*, **10.** 401, 1868 ; A. Villiers and F. Borg, *Bull. Soc. Chim.* (3), **9.** 486, 1893 ; *Compt. Rend.*, **116.** 989, 1893 ; H. C. Babbitt, *Journ. Anal. App. Chem.*, **7.** 165, 1893 ; A. von Lipowitz, *Pogg. Ann.*, **109.** 135, 1860 ; C. Friedheim, *Zeit. anorg. Chem.*, **4.** 275, 1893 ; T. Salzer, *Liebig's Ann.*, **187.** 322, 1877 ; G. P. Baxter and R. C. Griffin, *Amer. Chem. Journ.*, **34.** 204, 1905 ; T. S. Gladding, *Journ. Amer. Chem. Soc.*, **18.** 23, 1896.

[2] G. Chesneau, *Rev. Met.*, **5.** 237, 1908 ; *Principes Théoriques et Pratiques d'Analyse minérale*, Paris, 233, 1912

[3] G. P. Baxter, *Amer. Chem. Journ.*, **28.** 298, 1902.

[4] R. Fresenius, *Zeit. anal. Chem.*, **3.** 446, 1864 ; R. Fresenius, C. Neubauer, and E. Luck, *ib.*, **10.** 133, 1871 ; G. König, *ib.*, **10.** 305, 1871 ; E. Richters, *Dingler's Journ.*, **199.** 183, 1871.

ammonium chloride retards the precipitation,[1] and Richters has shown that the presence of ammonium sulphate acts in a similar manner. In these cases, a larger excess of ammonium molybdate must be added, or the results will be low.

Influence of Iron Salts.—If ferric salts be present, a comparatively large excess of ammonium molybdate is needed, even in the presence of ammonium nitrate; and if too little acid be present, a reddish crust which does not readily dissolve in ammonia may be formed. This is due to the formation of a ferric phosphomolybdate.[2] According to Meineke, a larger excess of nitric acid is also needed if much iron be present in the solution, in order to prevent the precipitation of iron with the ammonium phosphomolybdate; and Jüptner[3] proposes to use 6 per cent. of tartaric acid with the molybdate solution in order to prevent the precipitation of the iron.

Influence of Titanium and Vanadium.—The presence of titanium retards the precipitation of ammonium phosphomolybdate. For instance, two solutions, each containing the equivalent of 0·140 grm. of ammonium phosphomolybdate, furnished, in the presence of the equivalent of

Titanic acid	0·008	0·016	grm.
Ammonium phosphomolybdate . . .	0·122	0·118	grm.

Hence, there is a deficiency of 13 per cent. of P_2O_5 even in the presence of but 0·008 grm. of titanic acid. Pattinson[4] separates the titanium[5] before precipitating the phosphorus, in the following manner:—Reduce the ferric to ferrous sulphate; add a saturated solution of ammonium alum, and then an excess of ammonia. The precipitate contains aluminium phosphate, aluminium hydroxide, and titanic oxide. Fuse the ignited precipitate with sodium carbonate, and extract the fused mass with water. Sodium phosphate and aluminate dissolve, while sodium titanate remains insoluble. "As a rule, one fusion suffices to separate all the phosphoric acid from the titanic acid." Vanadium is carried down quantitatively by the phosphomolybdate precipitate, which has then different properties from the ordinary precipitate, for it is more soluble in nitric acid, and in the ordinary washing solutions.[6]

Influence of Arsenic Oxide.—If arsenic be present, and the temperature of the solution be too high, ammonium arsenomolybdate will contaminate the precipitate of ammonium phosphomolybdate, and, later on, the second precipitate. A temperature of 45° is generally considered a safe upper limit,[7] but if much arsenic be present, the phosphomolybdate precipitate will even then be contaminated. For instance, Jorgensen found the following amounts of arsenic in the precipitated phosphomolybdate after standing 24 hours at 37°:

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[1] C. Meineke (*Chem. Ztg.*, **20.** 113, 1896) says that ammonium chloride does not retard the precipitation.

[2] G. Chesneau, *Rev. Met.*, **5.** 237, 1908; G. Arth, *Bull. Soc. Chim.* (3), **2.** 324, 1890; *Chem. News*, **62.** 155, 1890; C. Meineke, *Rep. Anal. Chem.*, **6.** 304, 1886; E. Wolff, *Zeit. anal. Chem.*, **3.** 94, 1864; R. Fresenius, *ib.*, **3.** 446, 1864; P. Schweitzer, *ib.*, **9.** 85, 1870; J. V. Janovsky, *ib.*, **11.** 157, 1872; S. W. Johnson, *Journ. Amer. Chem. Soc.*, **16.** 462, 1894; L. von Szell, *Landw. Ver. Stat.*, **55.** 341, 1901.

[3] R. Woy, *Chem. Ztg.*, **21.** 470, 1897; H. F. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **42.** 471, 1894.

[4] J. and H. S. Pattinson, *Journ. Soc. Chem. Ind.*, **14.** 443, 1895; P. H. Waller, *Journ. Amer. Chem. Soc.*, **20.** 513, 1898.

[5] In silicate analyses, titanium phosphate separates with the silica during the evaporation for silica.

[6] H. Brearley and F. Ibbotson, *The Analysis of Steel-Works Materials*, London, 163, 1902; J. R. Cain and J. C. Hostetter, *Journ. Ind. Eng. Chem.*, **4.** 250, 1912.

[7] H. C. Babbitt, *Journ. Amer. Chem. Soc.*, **6.** 381, 1884; M. Frank and F. W. Hinrichsen, *Stahl Eisen*, **28.** 295, 1908; M. Seligsohn, *Journ. prakt. Chem.* (1), **67.** 481, 1856; H. Seyberth, *Ber.*, **7.** 391, 1874; W. Gibbs, *Amer. Chem. Journ.*, **7.** 313, 1886; E. D. Campbell, *Journ. Anal. App. Chem.*, **7.** 2, 1893.

Original solution contained . . .	0·0033	0·0066	0·0143	grm. arsenic acid.
Precipitate contained	0·0013	0·0029	0·0040	grm. arsenic acid.

It is therefore advisable to remove the arsenic, if present, either by means of hydrogen sulphide (Fresenius) or by evaporation with hydrochloric and oxalic acids (Campbell).[1]

Influence of Silica.—It is generally agreed that silica should be removed, since it is liable to be precipitated in the form of ammonium silicomolybdate,[2] which does not settle so quickly as the corresponding phosphorus compound. According to Isbert and Stutzer,[3] the silicomolybdate can be removed from the phosphomolybdate by washing with ice-cold water, in which the former is easily soluble, the latter almost insoluble. The silica is, however, usually removed by evaporation before the separation of the phosphorus.

Influence of Organic Matter.—Carbonaceous matters are generally supposed to hinder the precipitation of the ammonium phosphomolybdate precipitate;[4] so also are the organic acids—tartaric and oxalic. Jüptner, however, says that this is not the case, and even recommends the addition of tartaric acid with the ammonium molybdate solution to retard the precipitation of the iron.

§ 309. The Gravimetric Determination of Phosphorus—Woy's Process.

Woy's method[5] of separating phosphorus in the form of ammonium phosphomolybdate is one of the best. The phosphoric oxide in an aliquot portion[6] of the acid solution of the pyrosulphate fusion obtained in the regular course of the typical silicate analysis (page 186) may be determined by this process; or separated by Joulie's process (page 603), and determined colorimetrically.

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[1] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1.** 421, 1876; E. D. Campbell, *Journ. Anal. App. Chem.*, **6.** 370, 1890; G. Jorgensen, *Mem. Acad. Roy. Soc. Danemark* (7), **2.** 141, 1905; P. Champion and H. Pellet, *Bull. Soc. Chim.* (2), **27.** 6, 1877; *Chem. News*, **35.** 115, 1877; G. Maderna, *Atti Accad. Lincei*, **19.** 15, 1910.

[2] T. Petersen, *Verhandl. Geol. Reichsanst.*, 80, 1869; W. Knop, *Chem. Centr.* (2), **2.** 691, 861, 1857; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1.** 411, 1903; J. H. Vogel, *Repert. Anal. Chem.*, **7.** 568, 469, 1887; E. Richters, *Dingler's Journ.*, **199.** 183, 1871; R. W. Atkinson, *Chem. News*, **35.** 127, 1887. On the other hand, E. Thilo (*Chem. Ztg.*, **11.** 193, 1889), E. R. E. Müller (*ib.*, **35.** 1201, 1911), E. H. Jenkins (*Journ. prakt. Chem.* (2), **13.** 237, 1876), G. Kennepohl (*Chem. Ztg.*, **11.** 1089, 1887), C. Meineke (*Repert. Anal. Chem.*, **6.** 303, 325, 1886), J. Hanamann (*Zeit. Landw. Vers. Ost.*, **3.** 53, 1900), and H. C. Sherman and H. S. J. Hyde (*Journ. Amer. Chem. Soc.*, **22.** 652, 1900) consider that no notice need be taken of the silica. For *the separation of phospho- and silico-molybdates*, see P. G. Mélikoff, *Compt. Rend.*, **153.** 1478, 1911. The method is to digest the precipitate by molybdic solution with "permolybdate reagent" four times during 24 hours. Filter. Destroy the hydrogen peroxide by heating, and precipitate the phosphoric acid in the filtrate as usual. The "permolybdate reagent" is made by mixing equal volumes of 30 per cent. hydrogen peroxide and 15 per cent. ammonium nitromolybdate. The method is also used for *the separation of phosphoric and colloidal silicic acids*—P. G. Mélikoff and M. Becaia, *ib.*, **154.** 775, 1912; *Chem. Ztg.*, **36.** 617, 1912; P. G. Mélikoff, *Journ. Russ. Phys. Chem. Soc.*, **44.** 605, 1912.

[3] A. Isbert and A. Stutzer, *Zeit. anal. Chem.*, **26.** 583, 1887; *Chem. News*, **57.** 211, 1888.

[4] F. Hundeshagen, *Zeit. anal. Chem.*, **28.** 164, 1899; J. König, *ib.*, **10.** 305, 1871; E. Richters, *Dingler's Journ.*, **199.** 183, 1871; V. Eggertz, *Journ. prakt. Chem.* (1), **79.** 496, 1860; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **42.** 471, 1894; R. Woy, *Chem. Ztg.*, **21.** 470, 1897; C. Reichard, *ib.*, **27.** 833, 1903; R. Hamilton, *Journ. Soc. Chem. Ind.*, **10.** 904, 1891; G. Maderna, *Atti Accad. Lincei*, **19.** 827, 1910; A. Tamm, *Chem. News*, **49.** 208, 1884; M. Schild, *Chimiste*, **3.** 25, 1912.

[5] R. Woy, *Chem. Ztg.*, **21.** 441, 469, 1897; A. H. Meade, *Chem. News*, **101.** 241, 1910; G. B. van Kampen, *Chem. Weekblad*, **3.** 376, 1906.

[6] Or in the portion used for the determination of iron or titanium.

An aliquot portion,[1] say 100 c.c., of the solution of the pyrosulphate fusion (page 186) is neutralised with ammonia, and evaporated, if necessary, to about 50 c.c.[2] Add concentrated ammonia until a precipitate forms which does not disappear on standing; add 3 c.c. of concentrated nitric acid; add, say, 15 c.c. of ammonium nitrate,[3] so that the solution has between 5 and 15 per cent. of ammonium nitrate.[4] Place a thermometer in the liquid. Heat the solution to about 70°. Raise the thermometer about 2 inches above the level of the liquid in the beaker, and pour rapidly into the solution, say, 20 c.c. of ammonium molybdate[5] down the stem of the thermometer, using it as a glass rod. Agitate the liquid thoroughly. The yellow precipitate separates more thoroughly in hot solutions. Keep the solution at 70° for about half an hour. Decant through, say, a 7- or a 9-cm. filter paper, and wash the precipitate[6] by decantation[7] (about six times) with a mixed solution (about 50 c.c.) of equal volumes of the ammonium molybdate solution, ammonium nitrate, and nitric acid (1 : 2), until no permanent precipitate[8] separates from a drop of the wash-liquid on standing.[9] The precipitate is now distributed between the beaker and the filter paper. Place the beaker with the precipitate beneath the funnel, and dissolve the precipitate

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[1] If possible, no more solution should be taken than is equivalent to 0·1 grm. of P_2O_5. If more than this amount be present, take an aliquot portion and dilute to, say, 50 c.c.

[2] Most other solutions are treated in a similar manner. Arsenic is supposed to be absent.

[3] AMMONIUM NITRATE SOLUTION.—Dissolve 320 grms. of ammonium nitrate in water and make the solution up to a litre.

[4] The following table gives the relative proportions of ammonium molybdate, nitric acid, and ammonium nitrate to be used:—

Table LXIX.—Composition of Mother Liquid for the Precipitation of Ammonium Phosphomolybdate.

P_2O_5.	Ammonium molybdate.	Ammonium nitrate.	Nitric acid.
grm.	c.c.	c.c.	c.c.
0·1	120	30	19
0·01	15	20	10
0·005	15	20	10
0·002	10	15	5
0·001	10	15	5

When 0·5 grm. of substance is in question, every per cent. of P_2O_5 in the original sample requires 5 c.c. of the molybdate solution (T. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 361, 1911).

[5] AMMONIUM MOLYBDATE SOLUTION.—Dissolve 34·34 grms. of ammonium heptamolybdate —$(NH_4)_6Mo_7O_{24}.4H_2O$—in water and make the solution up to a litre ($\frac{1}{6}$E). 1 c.c. is nearly equivalent to 0·001 grm. P_2O_5. Do not make a large stock to be stored a long time. Note that common ammonium molybdate of commerce is not $(NH_4)_2MoO_4$, but $(NH_4)_6Mo_7O_{24}.4H_2O$. The gradual precipitation of molybdic acid is avoided by storing the solution in green glass bottles to cut off heat rays from light—W. Heike, *Stahl Eisen*, 29. 1446, 1911. For the properties of molybdate solutions, see papers cited above and A. L. Winton, *Journ. Amer. Chem. Soc.*, 18. 445, 1896; M. Kupferschläger, *Bull. Soc. Chim.* (2), 36. 644, 1881.

[6] In washing, the yellow precipitate often has a tendency to crawl above the top of the paper. Hence, the paper should fit the funnel closely, so that the portion which crawls will not be lost.

[7] There is no need to transfer all the precipitate from the beaker to the filter paper when a second precipitation is to be made.

[8] Pure water decomposes the precipitate. If a yellow precipitate should separate in the washings on standing, all the phosphorus was not precipitated. In that case, the filtered liquid must be treated with more ammonium molybdate, filtered, and washed again. A *white* precipitate of molybdic acid or ammonium tetramolybdate can be ignored.

[9] E. Raben (*Zeit. anal. Chem.*, 47. 546, 1908) washes until the wash-water gives no precipitate with potassium ferrocyanide.

on the filter paper with dilute ammonia ($2\frac{1}{2}$ per cent.). If all the precipitate in the beaker does not dissolve, pour more ammonia into the beaker.[1] Wash the filter paper half a dozen times with the $2\frac{1}{2}$ per cent. ammonia. The liquid in the beaker will now occupy about 50–100 c.c. It contains practically all the phosphoric acid, some molybdic acid, and ammonium nitrate in ammoniacal solution.[2] The phosphorus may be determined in several different ways. Reprecipitation as ammonium magnesium phosphate or as ammonium phosphomolybdate will give satisfactory results.[3]

310. The Reprecipitation as Ammonium Magnesium Phosphate.

Add, say, 10 c.c.[4] of magnesia mixture[5] to the hot[6] ammoniacal solution of the washed ammonium phosphomolybdate in 2·5 per cent. ammonia solution.

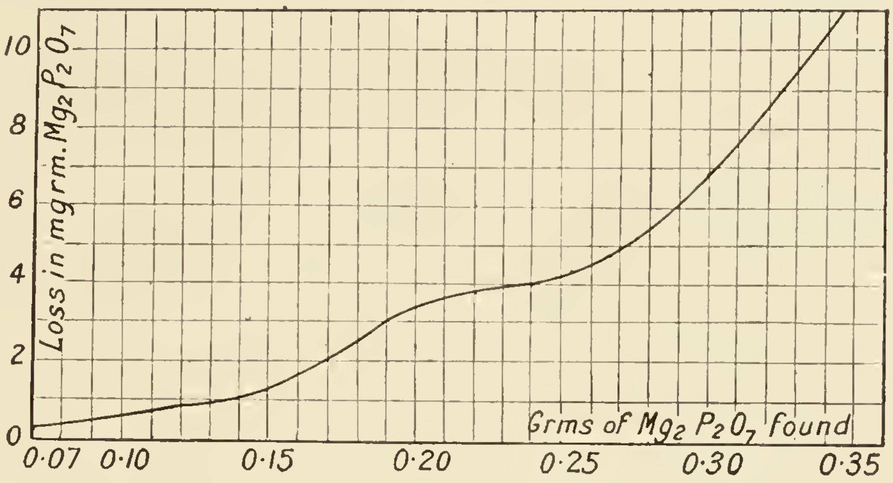

FIG. 189.—Neubauer's correction chart.

The addition is made very slowly, drop by drop, with constant stirring.[7] Let the mixture stand about 3 hours. Wash and ignite the precipitate as described for the determination of magnesia (page 218), and use Table XCI.

Neubauer's Correction.—It is not possible to precipitate pure ammonium magnesium phosphate from the solution of the ammonium phosphomolybdate[1] either by nearly neutralising the solution with hydrochloric acid before adding the magnesia mixture, or by adding magnesia mixture drop by drop, with constant stirring, to the ammoniacal solution. The latter process gives the better results, and Neubauer recommends the use of a correction chart which gives the amount, in milligrams, of P_2O_5 lost for different amounts (in grams) of $Mg_2P_2O_7$ finally obtained. Neubauer's chart is shown in fig. 189. It is used in the following manner:—Suppose 0·0959 grm. of $Mg_2P_2O_7$ has been obtained, then 0·4 mgrm. of $Mg_2P_2O_7$ has been lost in the determination. Hence, $0·0959 + 0·0004 = 0·0963$ grm. $Mg_2P_2O_7$ represents the weight of $Mg_2P_2O_7$ which would have been obtained if there had been no loss from this cause.

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[1] If the liquid in the beaker remains turbid, acidify with nitric acid, add a small crystal of citric acid, and, finally, ammonia until the liquid is alkaline. If the liquid be still turbid, filter, ignite in a platinum crucible, fuse with a little sodium carbonate, dissolve the cake in water, acidify with nitric acid, and add it to the rest of the solution.

[2] For error due to phosphorus in the glass beakers, etc., see A. Vita, *Stahl Eisen*, **32**. 1352, 1912.

[3] RECOVERY OF MOLYBDENIUM RESIDUES.—R. Fresenius, *Zeit. anal. Chem.*, **10**. 204, 1871; F. Muek, *ib.*, **10**. 307, 1871; **8**. 377, 1869; O. Maschke, *ib.*, **12**. 380, 1873; H. Uelsmann, *ib.*, **16**. 52, 1877; E. Reichardt, *Arch. Pharm.* (3), **2**. 232, 1873; A. Gawalovski, *Chem. News*, **75**. 98, 1897; *Oester. Chem. Ztg.*, **1**. 385, 1898; A. Börntrager, *Deut. Chem. Ztg.*, **9**. 10, 1894; *Chem. News*, **70**. 224, 1894.

[4] As many c.c. are needed as there are centigrams of P_2O_5 in the solution.

[5] MAGNESIA MIXTURE.—Dissolve 55 grms. of crystallised magnesium chloride ($MgCl_2 . 6H_2O$) and 70 grms. of ammonium chloride in 650 c.c. of water. When all is dissolved, make the solution up to a litre with concentrated aqueous ammonia. The solution is about $\frac{1}{2}$E strength. M. Brassier, *Ann. Chim. Phys.* (4), **7**. 355, 1866; A. L. Winton, *Journ. Amer. Chem. Soc.*, **18**. 445, 1896. G. Loges (*Chem. Ztg.*, **8**. 1743, 1884) uses magnesium ammonium chloride, which is not hygroscopic like magnesium chloride: 70 grms. magnesium ammonium chloride; 55 grms. ammonium chloride; make up to a litre with $2\frac{1}{2}$ per cent. ammonia. Magnesia mixture acts slowly on glass bottles—L. L. de Koninck, *Chem. Ztg.*, **19**. 450, 1895. Magnesia mixture containing magnesium sulphate instead of magnesium chloride is liable to give precipitates contaminated with basic magnesium sulphates. See page 218.

[6] According to O. Foerster (*Chem. Ztg.*, **16**. 109, 1892; *Chem. News*, **67**. 143, 1893), the solution should be heated before adding the magnesia mixture. Otherwise, the washing of the precipitate is very difficult.

[7] The precipitate should be white and crystalline. If it be red and flaky, the results will be inaccurate. If the phosphorus be finally weighed as magnesium pyrophosphate—$Mg_2P_2O_7$—traces of molybdic acid may contaminate the precipitate, even after two precipitations of the ammonium magnesium phosphate—A. A. Blair, *Chem. News*, **56**. 246, 1887; A Gawalovski, *Oester. Chem. Ztg.*, **1**. 385, 1890.

§ 311. The Reprecipitation as Ammonium Phosphomolybdate.

Add 20 c.c. of ammonium nitrate solution and 1 c.c. of ammonium molybdate to the ammoniacal solution of the ammonium phosphomolybdate first precipitated.[2] Heat the solution until gas bubbles begin to form, and add 20 c.c. of hot nitric acid gradually, with constant stirring. After standing 10 minutes, filter through a Gooch's crucible, and wash with the mixture previously employed until no brown coloration is produced when a drop of the filtrate is brought in contact with a solution of potassium ferrocyanide. Dry[3] the yellow precipitate of $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ in a current of air at 160°–180° in, say, a Paul's oven (fig. 127) to a constant weight,[4] and weigh as $(NH_4)_3PO_4.12MoO_3$.[5] In that case, the weight of the precipitate multiplied by 0·03782 represents the weight of the P_2O_5 in the sample taken for analysis.[6]

§ 312. Rapid Processes for Estimating the Ammonium Phosphomolybdate.

In order to shorten the time required for the determination of phosphorus in terms of ammonium phosphomolybdate, the amount of molybdenum precipitated is sometimes determined by volumetric methods.[7] In these it is assumed that the precipitated phosphomolybdate has a constant composition, and that a definite amount of molybdenum represents a definite amount of phosphorus. In Emmerton's process, the yellow precipitate is dissolved in, say, 5 c.c. of concentrated aqueous ammonia and 20 c.c. of water. Pour this mixture through the filter paper containing the precipitate, and wash the paper as indicated above. About 60 c.c. of liquid are so obtained. Add, say, 10 c.c. of concentrated sulphuric acid,[1] and at once reduce the molybdenum trioxide—MoO_3—to the green oxide—Mo_2O_3 or $Mo_{12}O_{19}$ [2] by means of metallic zinc (say, in the reductor, page 191). The solution, if necessary, is rapidly filtered from the undissolved zinc, and titrated with potassium permanganate,[3] when the green oxide is oxidised to MoO_3. The greenish-coloured solution becomes nearly colourless, and finally pink, characteristic of potassium permanganate. The oxidation is represented in symbols:

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[1] H. Neubauer, *Ueber die Zuverlässigkeit der Phosphorsäurebestimmung als Magnesiumpyrophosphat*, Rostock, 1893; G. Jorgensen, *Mem. Acad. Roy. Soc. Danemark* (7), **2**. 141, 1905; O. Abesser, W. Jani, and M. Märcker, *Zeit. anal. Chem.*, **12**. 239, 1873; B. Peitzsch, W. Rohn, and P. Wagner, *ib.*, **19**. 444, 1880; B. W. Kilgrove, *Journ. Amer. Chem. Soc.*, **16**. 793, 1894; G. Jorgensen, *Zeit. anal. Chem.*, **50**. 337, 1911.

[2] The phosphorus should not be precipitated first by the magnesia mixture, but be first precipitated by the molybdate process. This ensures a definite amount of ammonia and ammoniacal salts in the solution, and thus leads to concordant results.

[3] E. Raben (*Zeit. anal. Chem.*, **47**. 546, 1908) finishes the washing with warm 70 per cent. alcohol; then with absolute alcohol; then with 10 c.c. of ether. He dries the precipitate at 110°–120°, and weighs as $(NH_3)_3PO_4.12MoO_3$. A. Carnot, *Compt. Rend.*, **106**. 105, 1893; *Chem. News*, **67**. 101, 1893; A. Villiers and F. Borg, *ib.*, **67**. 313, 1893; *Compt. Rend.*, **106**. 989, 1893; C. Reichard, *Pharm. Zentralhalle*, **52**. 1314, 1911; N. von Lorenz, *Oester. Chem. Ztg.*, **14**. 1, 1911; G. Jorgensen, *Zeit. angew. Chem.*, **24**. 542, 1911; H. Neubauer and F. Lücker, *Zeit. anal. Chem.*, **51**. 161, 1912.

[4] The precipitate is somewhat hygroscopic, and the desiccator should have fresh concentrated sulphuric acid, not calcium chloride, otherwise the precipitate might gain in weight.

[5] If the precipitate appears green, add a small crystal of ammonium nitrate and re-heat. The precipitate then becomes uniformly yellow.

[6] If desired, the precipitate may be ignited to redness until the resulting $24MoO_3.P_2O_5$ has a homogeneous black colour. The ignited precipitate is not specially hygroscopic.

[7] J. Macagno, *Gaz. Chim. Ital.*, **4**. 567, 1874; *Chem. News*, **31**. 197, 1875; A. Grete, *Ber.*, **21**. 2762, 1888; F. A. Emmerton, *Trans. Amer. Inst. Min. Eng*, **15**. 93, 1887; T. M. Drown and P. W. Shimer, *ib.*, **10**. 137, 1882; P. W. Shimer, *ib.*, **17**. 100, 1889; T. M. Drown, *ib*, **18**. 90, 1890; C. Jones, *ib.*, **17**. 411, 1889; **18**. 705, 1890; *Chem. News*, **62**. 220, 231, 1890; D. L.

$$5Mo_2O_3 + 6KMnO_4 = 10MoO_3 + 3K_2O + 6MnO,$$

or,

$$5Mo_{12}O_{19} + 34KMnO_4 = 60MoO_3 + 17K_2O + 34MnO.$$

The calculations are as follow:—1 grm. of $KMnO_4$ represents 1·5188 grms. of MoO_3 if the reduction has been to Mo_2O_3; and 1·60083 if the reduction has been to $Mo_{12}O_{19}$. But since the ratio of $P_2O_5 : MoO_3$ is as 1 : 24, every gram of MoO_3 represents 0·04108 grm. of P_2O_5. Hence, 1 grm. of $KMnO_4$ represents 0·06239 grm. of P_2O_5 if the reduction has been to Mo_2O_3; and 0·06576 grm. of P_2O_5 if the reduction has been to $Mo_{12}O_{19}$. In a given titration, therefore, if 20 c.c. of potassium permanganate solution contain 1 grm. of $KMnO_4$ per litre, 1 c.c. of the solution represents 0·00006239 grm. of P_2O_5, or 20 c.c. represent $20 \times 0·00006239 = 0·00125$ grm. of P_2O_5 in the sample undergoing titration.[4]

Pemberton washes the precipitate of ammonium phosphomolybdate free from nitric acid, and dissolves the precipitate in standard alkali. The excess of alkali is titrated with standard acid, with phenolphthalein as indicator. The reaction is represented: $2(NH_4)_3PO_4 . 12MoO_3 + 46KOH =$ etc.[5]

Osmond dissolves the ammonium phosphomolybdate,[6] collected on an

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Randall, *ib.*, **97**. 113, 1908; *Amer. J. Science* (4), **24**. 313, 1907; O. F. von der Pfordten, *Zeit. anal. Chem.*, **23**. 432, 1884; A. Werncke, *ib.*, **14**. 1, 1875; H. Pemberton, *Journ. Franklin Inst.* (3), **83**. 184, 1882; *Chem. News*, **46**. 4, 1882; *Journ. Amer. Chem. Soc.*, **16**. 278, 1894; A. A. Blair and J. E. Whitfield, **17**. 747, 1895; W. A. Noyes and E. D. Frohman, *ib.*, **16**. 533, 1894; W. A. Noyes and J. S. Royse, *ib.*, **17**. 129, 1895; C. B. Dudley and F. N. Pease, *ib.*, **16**. 224, 1894; R. A. Mahon, *ib.*, **19**. 792, 1897; O. S. Doolittle and A. Eavenson, *ib.*, **16**. 234, 1894; G. Auchy, *ib.*, **18**. 955, 1896; B. W. Kilgore, *ib.*, **16**. 765, 1894; **17**. 741, 950, 1895; E. D. Campbell, *Journ. Anal. App. Chem.*, **1**. 370, 1887; B. W. Kilgore, *Bull. U.S. Agric. Dept.* (*Chem.*), **43**. 68, 1894; G. P. Baxter, *Amer. Chem. Journ.*, **28**. 298, 1902; **34**. 204, 1905; J. G. Fairchild, *Journ. Ind. Chem. Eng.*, **4**. 520, 1912. See page 415.

[1] The smaller the amount of sulphuric acid in the solution, the quicker the reduction.

[2] Complete reduction to Mo_2O_3 is difficult, and the reduced oxide has, in consequence, been represented by different formulæ—Mo_2O_3 (Pfordten); $Mo_{12}O_{19}$ (Emmerton); $Mo_{24}O_{37}$ (Blair and Whitfield).

[3] The permanganate should always be standardised with a known amount of phosphorus in combination.

[4] If the solution has been standardised for a given amount of P_2O_5, these calculations are not needed.

[5] C. B. Williams, *Journ. Amer. Chem. Soc.*, **17**. 924, 1895; A. Emmerling, *Chem. News*, **57**. 15, 1888; *Zeit. anal. Chem.*, **26**. 244, 1887; F. Hundeshagen, *ib.*, **28**. 141, 1889; L. Fricke, *Stahl Eisen*, **26**. 279, 1906; J. M. Krasser, *Zeit. Nahr. Genuss.*, **21**. 198, 1911; L. T. Bowser, *Amer. Chem. Journ.*, **45**. 230, 1911; F. Hundeshagen, *Zeit. öffent. Chem.*, **17**. 283, 302, 322, 1911; M. Wagenaar, *Pharm. Weekblad*, **48**. 845, 1911; J. G. Fairchild, *Journ. Washington Acad. Science*, **2**. 114, 1912.

[6] F. Osmond, *Bull. Soc. Chim.* (3), **47**. 745, 1887; *Chem. News*, **56**. 160, 1887.

asbestos pad, in a Gooch's crucible, in a hydrochloric acid solution of stannic oxide.[1] The filtered solution is made up to 100 c.c., and the intensity of the colour is compared with that of a solution containing a known amount of the phosphomolybdate.

For certain purposes, a sufficiently close approximation to the amount of the precipitated ammonium phosphomolybdate can be obtained by measuring the volume of the precipitate collected in the graduated test tube of a centrifugal machine.[2]

§ 313. The Volumetric Determination of Phosphorus—Uranium Process.

Uranium acetate or nitrate reacts with phosphates in aqueous solution forming uranium phosphate. When all the phosphorus has been transformed to uranium phosphate, any further addition of the uranium salt will give a solution which furnishes a reddish-brown coloration when brought in contact with a solution of potassium ferrocyanide. These facts are utilised in a volumetric process. The reaction takes place somewhat slowly in the cold, and, in consequence, the titration is generally finished with hot solutions—about 90°. The reaction is supposed to be slower in the presence of acetates, and hence the acetates should be kept as low as possible. But even when uranium nitrate is used for the titration, there is a considerable amount of acetate present. The amount of acetate added with uranium acetate is but a small fraction of the whole. Consequently, it makes little difference whether uranium nitrate or acetate is used in the titration.[3] When the uranium solution is to be employed for titrating calcium phosphates, bone ash, etc., it is generally standardised against a solution of calcium phosphate of known strength.

The Standard Solutions.—Make a standard solution of pure calcium phosphate—$Ca_3(PO_4)_2$—by dissolving 10 grms. of normal calcium phosphate in a little nitric acid, and dilute the solution to 1 litre.[4] Then dissolve 40 grms. of uranium nitrate or 35 grms. of uranium acetate in about 800 c.c. of water.

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[1] Dissolve 10 grms. of "tin crystals" in 80 c.c. of pure hydrochloric acid, and make the solution up to a litre.

[2] V. Eggertz, *Journ. prakt. Chem.* (1), **79**. 496, 1860; H. Wedding, *Stahl Eisen*, **7**. 118, 1887; M. Ukena, *ib.*, **7**. 407, 1887; M. A. von Reis, *ib.*, **9**. 1025, 1889; **10**. 1059, 1890; K. Bormann, *Zeit. angew. Chem.*, **3**. 638, 1889; C. Reinhardt, *Chem. Ztg.*, **15**. 410, 1891; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **43**. 203, 1895; J. Ohly, *Chem. News*, **76**. 200, 1897.

[3] F. Sutton, *Chem. News*, **1**. 97, 122, 1860; H. Neubauer, *Archiv Wiss. Heilkunde*, **4**. 228, 1893; C. Pincus, *Journ. prakt. Chem.* (1), **76**. 104, 1859; R. Arendt and W. Knop, *ib.* (1), **69**. 401, 415, 1856; K. Broockmann, *Rep. anal. Chem.*, **1**. 212, 1881; A. E. Haswell, *ib.*, **2**. 251, 1882 (the more uranium solution employed, the higher becomes its relative value); C. Mohr, *Zeit. anal. Chem.*, **19**. 150, 1880; *Chem. News*, **45**. 248, 1882; V. Edwards, *ib.*, **59**. 159, 1889; G. Guérin, *ib.*, **8**. 175, 1882; *Rep. anal. Chem.*, **3**. 157, 1883; O. Abesser, W. Jani, and M. Märcker, *Zeit. anal. Chem.*, **12**. 239, 1873; E. Kessel, *ib.*, **8**. 164, 1869; C. Leconte, *Compt. Rend.*, **29**. 55, 1849; W. Knop, *Chem. Centr.* (2), **1**. 737, 769, 1856; H. Rheineck, *Dingler's Journ.*, **200**. 383, 1870; A. Pavec, *Listy's Chemiké*, **1**. 313, 1875; W. Strecker and P. Schiffer, *Zeit. anal. Chem.*, **50**. 495, 1911; A. Vozarik, *Zeit. physiol. Chem.*, **76**. 433, 1912.

[4] The strength of the solution may be confirmed, if there be any doubt of the purity of the calcium phosphate, by precipitating according to the molybdate process (page 598). J. A. Muller (*Bull. Soc. Chim.* (3), **25**. 1000, 1901; *Chem. News*, **85**. 124, 1902) prefers crystallised dicalcium phosphate—$Ca_2H_2(PO_4)_2 . 4H_2O$—on account of its stability on exposure to the air, etc. If alkaline phosphates are to be titrated, potassium phosphate is used. For this purpose, dissolve 9·585 grms. of monopotassium phosphate—KH_2PO_4—in a litre of water. The solution is standardised by evaporating a known volume of the solution to dryness in a platinum dish. Ignite the residue at the full heat of a Bunsen flame, and weigh as KPO_3. Or the phosphorus in a known volume may be determined by the magnesium process (page 597).

Add a few drops of ammonia, when a slight turbidity will be produced. Then add just enough acetic acid to clear the solution, and make up to a litre.[1]

Standardisation of the Uranium Solution.—Take 50 c.c. of the calcium phosphate solution, and add 10 c.c. of ammonium acetate,[2] and run the uranium acetate from a burette until a drop of the clear solution gives the first sign of a permanent reddish-brown coloration with a little powdered (solid) potassium ferrocyanide[3] on a white plate.[4] The solution must be well agitated after each addition of the uranium solution. Then heat the solution to boiling,[5] when a drop will no longer react with the ferrocyanide.[6] Add more uranium solution until the brown colour with the ferrocyanide is again developed. The result of this titration enables the strength of the uranium solution to be represented in terms of the calcium phosphate.

Evaluation of Bone Ash.—Supposing that bone ash is to be analysed, dissolve between 3 and 4 grms. of the bone ash in dilute nitric acid (10 per cent.).[7] Add ammonia to the filtrate and washings until a permanent precipitate is obtained. Redissolve the precipitate[8] in a little acetic acid, add 10 c.c. of ammonium acetate, and titrate the solution (occupying, say, 500 c.c.) with the uranium solution, as indicated above.

Calculation.—Suppose that 50 c.c. of standard phosphate contain 0·5 grm. of $Ca_3(PO_4)_2$, and n c.c. of the uranium solution are needed for the titration, obviously, 1 c.c. of the uranium solution represents $0·5/n$ of $Ca_3(PO_4)_2$. If w

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[1] The uranium salt should be free from uranium phosphate or ferric nitrate. Let the solution stand some days before it is standardised, otherwise the turbidity which sometimes develops, owing to the separation of uranium phosphate, may alter the strength of the solution. The less free acetic acid the better, since the solution is more sensitive in the absence of an excess of free acetic acid. The strength of the solution should be checked every three or four days.

[2] AMMONIUM ACETATE SOLUTION.—Dissolve 154 grms. ammonium acetate in water, add 100 c.c. of acetic acid (sp. gr. 1·04), and dilute the solution to a litre (2E). The object of the ammonium acetate is to prevent the formation of free nitric acid.

[3] Or a drop of a solution of 1·1 grms. of the same salt—potassium ferrocyanide—in 10 c.c. of water (E).

[4] For the method of titration with a "spot" indicator, see page 334. If an excess of uranium solution be added, a known amount of the standard phosphate solution may be added, and the uranium titration continued. An allowance may be made for the phosphate added. In shaking, avoid making the solution froth, since a drop of uranium falling on the froth does not readily mix with the liquid underneath. A drop of alcohol will generally dispel the froth.

[5] If the solution be heated before the greater part of the phosphoric acid has combined with the uranium, some calcium phosphate may be precipitated (R. Fresenius, C. Neubauer, and E. Luck, *Zeit. anal. Chem.*, **10.** 133, 1871; C. Schumann, *ib.*, **11.** 382, 1872).

[6] If a little uranium phosphate be removed with the rod in making the spot test, the ferrocyanide may be "browned" before the reaction is at an end. If the "spot" test gives a brown, add another four drops of the uranium solution. If the brown does not appear the moment the glass rod is removed, the first "browning" was not the end of the titration. This supplementary "four-drop test" should always be made. C. Mallot (*Archiv Pharm.*, **2.** 246, 1887) uses, as indicator, an aqueous ammoniacal solution of cochineal just decolorised with nitric acid. Titrate with this solution as an internal indicator until a permanent green is obtained—E. Starkenstein, *Biochem. Zeit.*, **32.** 235, 1911.

[7] The insoluble earthy and sandy matters may be filtered off in a Gooch's crucible, dried, and weighed.

[8] If iron and alumina be present, phosphates of these elements will be precipitated, and these remain insoluble in the acetic acid. In that case, filter the turbid solution. Titrate the filtrate as indicated in the text. Ignite and weigh the precipitate. If less than 0·01 grm. of the mixed phosphates be present, take half the weight as P_2O_5 and add the result to the P_2O_5 obtained by the titration. If over this amount of precipitate be present, the process is unreliable, or the P_2O_5 may be determined in the precipitate by the molybdate process (V. Edwards, *Chem. News*, **73.** 25, 71, 1896; G. H. Allibon, *ib.*, **73.** 47, 94, 1896). There is then no particular advantage in the volumetric process over, say, Woy's process. Other phosphates—*e.g.* cerium phosphate—may be precipitated if they be present—E. Damour and H. St C. Deville, *Instit.*, 69, 1858; *Compt. Rend.*, **59.** 272, 1864; J. Boussingault, *Ann. Chim. Phys.* (4), **22.** 457, 1871.

grms. of the bone ash be employed, and this requires m c.c. of the uranium solution, obviously the w grms. of bone ash contain $0{\cdot}5m/n$ grms. of $Ca_3(PO_4)_2$, or

$$100\frac{0{\cdot}5m}{wn} \text{ per cent. of } Ca_3(PO_4)_2.$$

Errors.—It will be noticed that a slight excess of uranium is required to produce a coloration with potassium ferrocyanide, since enough uranium must be added not only to precipitate the phosphoric oxide, but also to colour the ferrocyanide. This excess must be allowed for by working under constant conditions, and making a blank titration on a solution prepared as indicated above, for standardising the uranium, but excluding the phosphate, and always using the same volume of solution in the titration.

The most important sources of error in this titration are: (1) Mistaking transient for permanent "browning"—make sure, by means of the "four-drop test," that the red tint is not an illusory end point; (2) Error due to the removal of too small a drop to colour the ferrocyanide; (3) Error due to titrating too quickly and overreaching the end of the reaction; and (4) Error due to the retention of uranium solution by the froth, and touching the ferrocyanide with this.

The analysis should be made in duplicate, and no number should be accepted if it deviates appreciably from the others. It may be again emphasised that, while the agreement between the duplicates is a test of the accuracy of the work, it is not, as is sometimes supposed, an indication of the trustworthiness of the process. Some, expecting too much from this process, have given it up in disgust.

Owing to the almost invariable presence of appreciable amounts of alumina and iron, it may be advisable to first separate the phosphorus by means of ammonium magnesium citrate[1] before titrating with uranium nitrate. If organic matter be present, it should be removed by a preliminary incineration, since organic matter interferes with the uranium reaction. Arsenic, if present, should be removed by first passing a current of sulphur dioxide through the solution; boiling to remove the sulphur dioxide; and precipitating the arsenic with hydrogen sulphide.[2]

PURCHASING BONE ASH.—According to the "English Form of the Hamburg Contract," bone ash is invoiced as follows :—

> If the delivered bone ash contains BELOW 70 per cent. TRIBASIC PHOSPHATE OF LIME,[3] an allowance shall be made to the Buyers according to the following principle and scale :—
>
> For Ash below 70 % for every 1 % less, 1½ % phosphate less to be invoiced.
> ,, ,, 65 % ,, further 1 % ,, 2 % ,, ,, ,,
> ,, ,, 60 % ,, ,, 1 % ,, 3 % ,, ,, ,,
>
> For fractions, the allowance to be made on the same scale, for instance :—

69 %	invoiced as 68½ %	65 %	invoiced as 62½ %	61 %	invoiced as 54½ %
68½ ,,	,, 67¾ ,,	64½ ,,	,, 61½ ,,	60½ ,,	,, 53½ ,,
68 ,,	,, 67 ,,	64 ,,	,, 60½ ,,	60 ,,	,, 52½ ,,
67½ ,,	,, 66¼ ,,	63½ ,,	,, 59½ ,,	59½ ,,	,, 51 ,,
67 ,,	,, 65½ ,,	63 ,,	,, 58½ ,,	59 ,,	,, 49½ ,,
66½ ,,	,, 64¾ ,,	62½ ,,	,, 57½ ,,	58½ ,,	,, 48 ,,
66 ,,	,, 64 ,,	62 ,,	,, 56½ ,,	58 ,,	,, 46½ ,,
65½ ,,	,, 63¼ ,,	61½ ,,	,, 55½ ,,		and so on

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[1] H. Joulie, *Ann. Agronom.*, **11**. 97, 1885; *Chem. News*, **52**. 85, 1885; J. M. H. Munro, *ib.*, **52**. 86, 1885; L. Joulin, *ib.*, **27**. 228, 309, 314, 1873; C. Mène, *Compt. Rend.*, **76**. 1419, 1873.

[2] RECOVERY OF URANIUM RESIDUES.—W. Jani, *Chem. Centr.* (2), **2**. 231, 1871; W. Knop, *ib.* (2), **10**. 161, 1865; F. Strohmer, *Zeit. anal Chem.*, **17**. 84, 1878; A. Gawalovski, *ib.*, **15**. 292, 1876; E. Reichardt, *ib.*, **8**. 116, 1869; **13**. 310, 1874.

[3] That is, normal calcium phosphate—$Ca_3(PO_4)_2$.

Example.—Suppose 5 grms. of bone ash are taken for analysis. The solution is made up to 250 c.c., and 50 c.c. taken for a titration. Each 50 c.c. represents $w=1$ grm. of bone ash. Suppose $m=26{\cdot}6$ c.c. of the uranium solution are needed for the titration of this 50 c.c. of solution, and that $n=20$ c.c. of the uranium solution are needed for titrating 50 c.c. of the standard phosphate. Then, from the above formula,

$$\frac{100 \times 0{\cdot}5 \times 26{\cdot}6}{1 \times 20} = 66\tfrac{1}{2} \text{ per cent. } Ca_3(PO_4)_2.$$

If the phosphate be sold at 1s. 6d. per unit, a ton of the bone ash on the Hamburg scale is not invoiced at $66\frac{1}{2} \times 1\frac{1}{2} =$ £4, 19s. 9d., but at $64\frac{3}{4} \times 1\frac{1}{2} =$ £4, 17s. $1\frac{1}{2}$d. Of course the colour, freedom from specks, and working qualities of bone for pottery purposes are of more importance than "per cent. of normal phosphate."

§ 314. The Volumetric Determination of Phosphorus—Joulie's Magnesium Citrate Process.

Dissolve the substance under investigation in dilute hydrochloric acid, or in a mixture of nitric and hydrochloric acids if pyrites be present. If necessary, filter the solution.[1]

Separation of Phosphorus from Alumina and Iron as Magnesium Phosphate.—A portion of the clear solution, equivalent to 0·125 or 0·250 grm. of the phosphate, is pipetted into a beaker. Add 10 c.c. of magnesium citrate solution[2] and an excess of ammonia. The solution should be clear and only become turbid in a few seconds, especially after stirring.[3] Let the mixture stand under a bell-jar, to prevent loss of ammonia, overnight—that is, about 12–15 hours. Filter, first by decantation of the clear, and wash the precipitate with dilute ammonia (10 vols. water, 1 vol. ammonia). Four to six washings will suffice.[4]

Titration of the Magnesium Phosphate with Uranium Nitrate.—Dissolve the precipitate in a 10 per cent. solution of nitric acid. Allow the washings to run into the beaker in which the precipitation was made. Wash the filter paper with acidulated water. Put the filter paper in the beaker. Add dilute ammonia (1 : 10) until the solution is slightly turbid. Clear the turbidity with one or two drops of dilute nitric acid. Heat to boiling. Add 5 c.c. of ammonium acetate solution,[5] and titrate with the uranium acetate solution as described above.

§ 315. The Colorimetric Determination of Phosphorus.

Knight's[6] colorimetric process for the determination of phosphorus is based upon the intensity of the yellow colour of the phosphomolybdate in acid solutions. This colour test is very sensitive, since 0·000025 grm. of P_2O_5 can be recognised in cold solutions, and 0·0000025 grm. in hot solutions (80°). As with colorimetric processes generally, the colour is influenced by the composition of the solution in which the determination is made.[1] The principal difficulty is due to the influence of a small quantity of silica, which produces a potassium silicomolybdate with a yellow colour almost identical in tint with that of the potassium phosphomolybdate. It is therefore important to use reagents free from silica. The reagents must not be kept in glass vessels, owing to possible contamination by silica from the glass. The solutions should be kept in paraffin or cerasine bottles, or glass bottles coated internally with cerasine or paraffin. The absence of soluble silica in the reagents should be established by a blank test.

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[1] The removal of silica by evaporation is only necessary when the silicates are decomposed by the acid with the separation of gelatinous silica.

[2] Joulie's Magnesium Citrate Solution.—Citric acid 400 grms. is dissolved in pure magnesium carbonate 40 grms., caustic magnesia 20 grms., distilled water 500 c.c. Make the solution strongly alkaline with ammonia 600 c.c. If the solution be turbid, filter, and make the clear solution up to a litre.

[3] An immediate turbidity shows that insufficient citrate is present to hold all the iron and alumina in solution. In that case, start again and use 20 c.c. of the citrate solution. It is not sufficient to simply add more of the citrate solution to the turbid solution, because the precipitate of the phosphates of iron and alumina, once formed, does not readily redissolve. W. Simmermacher (*Chem. Ztg.*, **37**. 145, 1913) points out that the ammonium citrate should be added slowly, and a precipitate free from iron and silica can be obtained provided all the iron be in the form of citrate before the solution becomes alkaline.

[4] The wash-water then gives no precipitate with sodium phosphate.

[5] Sodium Acetate Solution.—A mixture of crystalline sodium acetate 100 grms. and glacial acetic acid 50 c.c. is made up to a litre with distilled water. The object of the sodium acetate solution is to prevent the development of free nitric or hydrochloric acid in the solution.

[6] J. W. Knight, *Analyst*, **5**. 195, 1882.

A standard solution of phosphate is made by dissolving 0·2453 grm. of pure, freshly crystallised monopotassium[2] phosphate—KH_2PO_4—in silica-free water and diluting the solution to a litre. Preserve the solution in a cerasine or paraffin bottle. Each cubic centimetre corresponds with 0·0001 grm. P_2O_5.

Standard Solution.—Dilute 10 c.c. of the standard potassium phosphate with, say, 80 c.c. of silica-free water. Add 10 c.c. of nitric acid (sp. gr. 1·07), and immediately add 8 c.c. of potassium molybdate solution.[3] Make the solution up to 1000 c.c.[4]

Test Solution.—Acidify a convenient portion—say, 25 c.c.—of the solution under investigation with 5 c.c. of nitric acid (sp. gr. 1·07), add 4 c c. of potassium molybdate solution, and make the solution up to, say, 50 c.c.

The Comparison.—Make the two solutions up immediately, and let them stand 20 minutes in order that the yellow tint of the phosphomolybdate may develop its maximum intensity. The intensities of the colours of the two solutions are now compared in a suitable colorimeter.[5] If the colour of the test solution be too strong for comparison, an aliquot portion is diluted in the usual manner. It is important to make sure that sufficient potassium molybdate is present to react with all the phosphate, by adding a further portion of the molybdate and diluting at the same time. Let the solution contain 5 c.c. of nitric acid, and 4 c.c. of the potassium molybdate, per 50 c.c. of solution. For smaller amounts of phosphorus, use a standard phosphate solution half the strength indicated above.

Errors.—If the solution under investigation be turbid, it should be filtered through biscuit-ware (page 631), evaporated to dryness, and then taken up with water and again filtered. Organic matter, if present, may produce a coloured solution. In that case, the organic matter must be destroyed or a correction must be made. Veitch destroys organic matter by ignition with magnesium nitrate and subsequent evaporation with nitric acid. Large amounts of ammonium salts—nitrate and chloride—intensify the colour, and hence lead to high results. Aluminium sulphate—$Al_2(SO_4)_3$—gives a dark, more or less opaque solution which spoils the determination. If less than 1 part of iron per 20 million parts of the solution be present, no particular harm can be noticed, but if larger amounts be present, the colour is intensified, and the result is vitiated unless the amount of iron be known and an allowance made for its effect. If iron and alumina be present, therefore, the phosphorus should be separated as magnesium phosphate by Joulie's process before the phosphorus determination is made.[1] Calcium nitrate, barium chloride, potassium nitrate, separately and mixed together, give no appreciable error. Nitric acid and potassium molybdate require attention. The standard and the test solutions should have approximately the same amounts of these two reagents, otherwise an appreciable error may be introduced. If the nitric acid solutions be passed through ordinary filter paper, there may be an error owing to the contamination of the solutions by phosphates and silica dissolved from the filter paper.

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[1] P. E. Alessandri, *Pharm. Centr.*, **35**. 170, 1865 ; C. Lepierre, *Bull. Soc. Chim.* (3), **15**. 213, 1896 ; A. Jolles and F. Neurath, *Monats. Chem.*, **19**. 5, 1898 ; A. Jolles, *Arch. Hygiene*, **34**. 22, 1899 ; A. Pagnoul, *Ann. Agronom.*, **25**. 549, 1899 ; O. Schreiner, *Journ. Amer. Chem. Soc.*, **26**. 806, 1904 ; **25**. 1056, 1903 ; O. Schreiner and B. E. Brown, *ib.*, **26**. 1463, 1904 ; F. P. Veitch, *ib.*, **25**. 169, 1903 ; J. G. Smith, *ib.*, **26**. 897, 1904 ; T. E. Hewitt, *ib.*, **27**. 121, 1905 ; C. Estes, *ib.*, **31**. 247, 1909 ; P. Veitch, *Chem. News*, **89**. 73, 89, 101, 1904.

[2] Sodium phosphate is difficult to deal with owing to efflorescence. J. A. Müller (*Bull. Soc. Chim.* (3), **25**. 1000, 1901) proposes the more stable microcosmic salt—$NaHNH_4PO_4 . 4H_2O$. The crystalline $CaHPO_4 . 2H_2O$ is quite stable in dry air or over phosphoric anhydride in a desiccator. It is a valuable standardising agent.

[3] POTASSIUM MOLYBDATE SOLUTION.—Dissolve 8 grms. of the salt in 50 c.c. of water, and make the solution up to 100 c.c. with nitric acid (sp. gr. 1·2). According to Jolles and Neurath, ammonium molybdate is liable to become turbid, and is not so sensitive as sodium or potassium molybdates. The coloration develops its maximum intensity at 80° in a short time. The colour with potassium molybdate develops more quickly, and is sharper and purer in tone than with sodium molybdate.

[4] N. Passerini (*Gaz. Chim. Ital.*, **41**. i. 182, 1911) recommends adding 2 c.c. of a cold saturated solution of gallic acid to the test glasses before the other solutions are added ; J. Pouget and D. Chouchak (*Bull. Soc. Chim.* (4), **5**. 104, 1909 ; (4), **9**. 649, 1911) use strychnine sulphate with the phosphomolybdate.

[5] Nessler's glasses may be used in place of the colorimeter. One Nessler's glass is filled up to the 20-c.c. mark or the 50-c.c. mark with the coloured solution under investigation. At the same time, other Nessler's glasses are filled to the same volume with solutions containing different amounts of the standard phosphate solution and the molybdate solution. By comparing the tint of the standard with the tint of the unknown solution, the amount of phosphoric acid in the solution can be determined.

§ 316. The Simultaneous Determination of Phosphorus and Silica.

Silica, as indicated above, is the great enemy of the colorimetric process for phosphates, since it produces a yellow-coloured silicomolybdate which was used by Jolles and Neurath for the colorimetric determination of silica. Woodman and Cayvan[2] found that the colour of the silicomolybdate required from $1\frac{1}{2}$ to $2\frac{1}{2}$ hours to develop its maximum intensity, and that the colour is about one-tenth of the intensity of the corresponding phosphomolybdate. This furnishes a means of correcting the determination of phosphorus for the influence of silica, and also to determine the amount of silica in the phosphate solution. If nitric acid and potassium molybdate be added to the solution as quickly as possible, a certain intensity of colour is developed by the silica. If, however, the ammonium molybdate be added an hour before adding the nitric acid, the intensity of the colour due to the silica is but half (0·49) as great as before. Phosphates give the same intensity as before under both conditions. Let x denote the amount of P_2O_5 present, and y the amount of silica present. The intensity of the colour produced by the silica is 1·25 times the intensity of the colour produced by the same amount of P_2O_5. Hence, $x + 1·25y$ will represent the joint effect of the silica and the phosphorus in terms of the phosphate standard, or

$$A = x + 1·25y \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value of A is determined by the colorimetric process indicated above.

If, in preparing the test solution indicated above, the addition of the nitric acid be deferred for one hour, and the comparison made 20 minutes afterwards, the colour produced by the silica will be but half its former value. Hence,

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[1] The magnesium phosphate is dissolved in nitric acid, etc. The magnesia precipitate (page 219) may also be evaluated by determining the amount of phosphorus it contains colorimetrically, and the corresponding amount of magnesia calculated in the usual manner. O. Schreiner and B. E. Brown, *Journ. Amer. Chem. Soc.*, **26**. 1463, 1904.

[2] A. J. Woodman and L. L. Cayvan, *Journ. Amer. Chem. Soc.*, **23**. 96, 1901 ; **24**. 735, 1902 ; A. G Woodman, *ib.*, **24**. 735, 1902 ; F. P. Veitch, *ib.*, **25**. 160, 1901 ; O. Schreiner, *ib.*, **25**. 1056, 1903 ; **26**. 808, 1904 ; **23**. 96, 1901 ; **24**. 755, 1902 ; A. T. Lincoln and P. Barker, *ib.*, **26**. 975, 1904.

$x + \frac{1}{2}(1\cdot25y)$ will represent the joint effect of the silica and the phosphorus in terms of the standard, or

$$B = x + \tfrac{1}{2}(1\cdot25y) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Multiply this equation by 2, and subtract the result from equation (1), and we get the value of x, that is,

$$\text{Amount of } P_2O_5 = 2B - A.$$

Similarly, by subtracting one equation from the other, we get the value of y, or

$$\text{Amount of } SiO_2 = 1\cdot6(A - B).$$

In illustration, suppose that we find the value A for PO_4 in the solution prepared by adding the ammonium molybdate and the nitric acid simultaneously to be 27, and the value of B for P_2O_5 in the solution when the nitric acid is added one hour after the ammonium molybdate to be 16. Obviously, from the above equations,

$$\text{Amount of } SiO_2 = 1\cdot6(27 - 16) = 17\cdot6.$$
$$\text{Amount of } P_2O_5 = 2 \times 16 - 27 = 9.$$

When the proportion of phosphorus to silica is small, Lincoln and Barker recommend the addition of, say, 5 c.c. of the standard phosphate solution to the test solution, and then conduct the process as indicated above. Due allowance is, of course, made for the phosphorus which has been added.

From what has been said above, it will be obvious that the colorimetric process may be employed for the determination of small quantities of soluble silica when phosphorus is absent.[1]

§ 317. The Analysis of Bone China Bodies.

The following numbers represent the ultimate percentage composition of a typical fired body, and show the kind of mixture now under investigation :

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5
38·0	16·0	1·2	1·0	22·0	2·5	1·5	18·0

With unfired bodies, free carbon, carbon dioxide, and the loss on ignition may also have to be determined. The amount of phosphoric oxide may or may not be sufficient to combine with all the alumina and ferric oxide. If the phosphoric oxide be in excess, lime and magnesia will be precipitated as phosphates along with the iron and aluminium phosphates. It is therefore necessary to modify the scheme of analysis indicated for clays. Several processes have been devised for dealing with the problem.[2] The following method is based on the assumption that the lime can be removed by precipitation as calcium sulphate in the presence of alcohol before the precipitation of aluminium and ferric phosphates by ammonia.[1] A great many of the details are carried out as described for clays, and there is no need to repeat full particulars.

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[1] A. Jolles and F. Neurath, *Zeit. angew. Chem.*, **11**. 315, 1898 ; R. Salvadori and G. Pellini, *Gaz. Chim. Ital.*, **30**. i. 191, 1900. H. Hermann (*Zeit. anal. Chem.*, **46**. 318, 1907) recommends potassium tungstate in place of potassium molybdate as a qualitative test for colloidal (soluble) silica—page 669.

[2] The ACETATE PROCESS is based on the assumption that the iron and aluminium phosphates are precipitated from a slightly acetic acid solution containing ferric oxide, alumina, lime, and phosphoric oxide by means of ammonium acetate. There are several modifications. The precipitate is contaminated with calcium phosphate—C. Glaser, *Zeit. anal. Chem.*, **31**. 383, 1892 ; W. Hess, *Zeit. angew. Chem.*, **7**. 679, 701, 1894 ; F. Wyatt, *The Phosphates of America*, New York, 150, 1892 ; R. T. Thomson, *Journ. Soc. Chem. Ind.*, **5**. 152, 1886 ; **15**. 868, 1896 ; *Chem. News*, **54**. 152, 1886. In the so-called CAUSTIC ALKALI PROCESS, the bases other than aluminium hydroxide are separated while the alumina is held in solution by the addition of an excess of caustic soda—L. Lasne, *Bull. Soc. Chim.* (3), **15**. 6, 118, 146, 1896 ; O. von Grüber, *Zeit. anal. Chem.*, **30**. 9, 1891 ; *Chem. News*, **63**. 146, 1891. In the OXALATE PROCESS, the solution remaining after the separation of the silica is mixed with sufficient tartaric acid to prevent the precipitation of alumina, etc., when ammonia is added to the solution. The lime is

1. *Separation of the Silica.*—Start with about a gram of the powdered substance[2] and digest it with aqua regia—hydrochloric acid (sp. gr. 1·2) 10 c.c., nitric acid (sp. gr. 1·12) 5 c.c.—on a water bath for about half an hour. Filter off the insoluble matter. Dry, and fuse the residue with sodium carbonate as indicated for clays (page 164). Take up the fused mass with dilute acid, mix the two solutions; evaporate to dryness;[3] take up with dilute hydrochloric acid; filter; wash; again evaporate to dryness; take up with acid; filter; wash until the washings are free from chlorides; ignite and weigh the separated silica (pages 168 and 169).

2. *Separation of the Lime as Calcium Sulphate.*—Evaporate the filtrate to about 50 c.c. Mix the solution with 10 c.c. of dilute sulphuric acid (1 : 5)[4] and about 150 c.c. of 95 per cent. of alcohol. In about three hours, filter off the precipitated calcium sulphate and wash with 50 per cent. alcohol until about 10 drops of the filtrate, diluted with an equal volume of water, do not redden a few drops of a solution of methyl orange. The precipitate may be[5] ignited and weighed as calcium sulphate—$CaSO_4$,—and the number so obtained, multiplied by 0·41186 or 0·4119, gives the equivalent of CaO; or the calcium sulphate may be redissolved in hydrochloric acid and reprecipitated by the oxalate process.

3. *Separation of Ferric Oxide, Alumina, and Phosphoric Oxide.*—Evaporate the

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then removed as calcium oxalate by the addition of ammonium oxalate. The filtrate is evaporated to dryness in a platinum dish and the organic matter destroyed by heat. The residue is taken up with hydrochloric acid, and the alumina, etc., separated as usual—L. Blum, *Zeit. anal. Chem.*, 39. 152, 1900. H. Immendorff (*Land. Ver. Stat.*, 34. 379, 1887) precipitates the lime as oxalate in a solution very slightly acidified with hydrochloric acid.

[1] E. Glaser, *Zeit. angew. Chem.*, 2. 636, 1889; R. Jones, *ib.*, 4. 3, 1891; J. H. Vogel, *ib.*, 4. 357, 1891; *Chem. Ztg.*, 15. 495, 1891; T. Meyer, *ib.*, 14. 1730, 1890; H. H. B. Shepherd, *Chem. News*, 63. 251, 1891; W. H. Krug and K. P. McElroy, *Journ. Amer. Chem. Soc.*, 17. 260, 1895; *Zeit. anal. Chem.*, 30. 206, 1891; T. M. Chatard, *Trans. Amer. Inst. Min. Eng.*, 21. 169, 1893; E. T. Teschemacher and J. D. Smith, *Chem. News*, 62. 84, 1890; N. Blattner and J. Brasseur, *ib.*, 76. 150, 1897; H. Herzog, *ib.*, 102. 25, 1910; *Journ. Ind. Eng. Chem.*, 1. 477, 1909; H. W. Wiley, *Principles and Practice of Agricultural Analysis*, Easton, Pa., 2. 224, 1908.

[2] Loss on Ignition.—For the volatilisation of phosphoric oxide during the calcination for loss on ignition, see E. Lautemann, *Liebig's Ann.*, 113. 240, 1860; S. Leavitt and J. A. Leclerc, *Journ. Amer. Chem. Soc.*, 30. 391, 617, 1908. A sample calcined at low redness gave 2·14 per cent. of ash, and at bright redness, 2·08 per cent. Another sample gave respectively 2·18 and 2·16 per cent. There was therefore no serious loss under the conditions of the experiment. G. Lechartier (*Compt. Rend.*, 109. 727, 1890) found the loss of phosphorus and also of sulphur is not serious if the operation be properly done. For the loss of sulphur during the calcination, see also G. S. Fraps, *Journ. Amer. Chem. Soc.*, 23. 199, 1901; E. Fleurent and L. Levi, *Bull. Soc. Chim.* (4), 9. 379, 1911.

[3] If the residue has a dark brown colour, organic matter is present, and it is best destroyed by conducting the next evaporation in a platinum dish, adding a little sodium nitrite, and heating the dried residue with a naked flame till the mass fuses to a colourless, viscid liquid. The dish is kept covered to prevent loss by spurting. Digest the cold mass with hydrochloric acid, evaporate to dryness, etc.

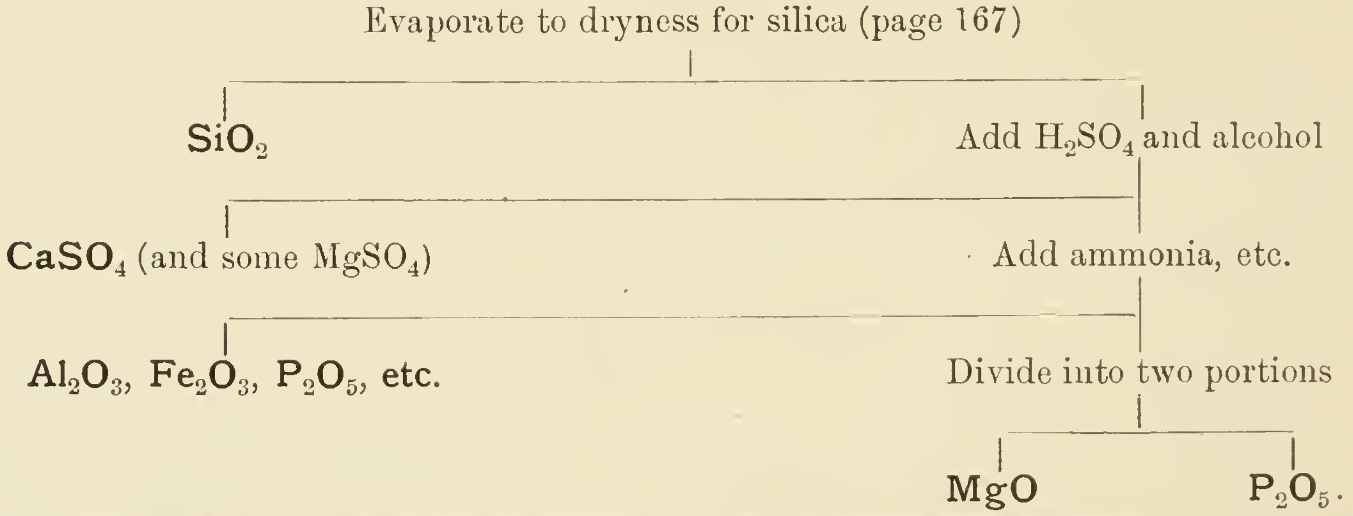
[4] Sulphates retard the complete precipitation of aluminium phosphate. According to F. P. Veitch (*Journ. Amer. Chem. Soc.*, 21. 414, 1897), the equivalent of "1·25 grm. H_2SO_4 prevents the complete precipitation of aluminium phosphate, and 2·75 grms. of H_2SO_4 gives a decided error." Hence, the amount of sulphuric acid should be kept as low as possible.

[5] Sometimes, particularly if a great excess of alcohol has been added, the calcium sulphate is discoloured. Again, if much magnesia be present in the sample, magnesium sulphate will be precipitated with the calcium sulphate. In each case, the calcium sulphate should be purified. The precipitated calcium sulphate may be dissolved in hot dilute hydrochloric acid, the lime precipitated as oxalate (page 213), and the filtrate added to the main solution; or the magnesia, if any be present, can be precipitated as ammonium magnesium phosphate in the usual manner (page 218).

filtrates to drive off the alcohol,[1] and oxidise any iron in the filtrate by adding a drop of bromine or some other oxidising agent. Add ammonium chloride and ammonia in slight excess. Boil the solution to expel ammonia.[2] Add a little more ammonia, and boil again. While the solution is hot, filter off the precipitated aluminium and ferric hydroxides and phosphates.[3] Wash with a hot (50°–60°) 5 per cent. solution of ammonium nitrate[4] until the washings are free from chlorine—about twenty washings are needed. Ignite[5] the precipitate from the ammoniacal solution with the residue left after the treatment of the ignited silica with hydrofluoric acid (page 169).[6] Weigh.[7] Fuse the precipitate with potassium pyrosulphate. Cool, and take up the cake with water. Filter off the "extra silica" and proceed for the titanium as indicated on page 203, and the phosphorus by Joulie's process.

4. *Separation of Magnesia and Phosphoric Oxide.*—The filtrate from the ammonia precipitate is evaporated to a small bulk,[8] and divided into two aliquot portions, and the magnesia determined in the one portion in the usual manner (page 218). If phosphoric acid be present in excess of that required for the formation of aluminium, titanium, and ferric phosphates, it can be determined as ammonium phosphomolybdate in the other portion (page 597). The phosphoric oxide (P_2O_5) here obtained is added to that separated from the ammonia precipitate, and the sum of the weights is multiplied by 2·1845. The product represents the corresponding amount of normal calcium phosphate —$Ca_3(PO_4)_2$. The weight of the magnesia here obtained is added to that separated from the calcium sulphate precipitate.

The method is summarised in the following scheme, starting from the mixed aqua regia solution and the hydrochloric acid solution from the sodium carbonate fusion :


Evaporate to dryness for silica (page 167)
SiO_2
Add H_2SO_4 and alcohol
$CaSO_4$ (and some $MgSO_4$)
Add ammonia, etc.
Al_2O_3, Fe_2O_3, P_2O_5, etc.
Divide into two portions
MgO
P_2O_5.

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[1] The alcohol may be recovered by connecting the flask containing the solution with a Liebig's condenser, and subsequently distilling the alcohol from soda lime.

[2] The boiling is said to help to prevent the contamination of the ferric and aluminium phosphates by magnesia later on.

[3] Also manganese or titanium phosphates, if titanium or manganese salts be present. In that event, the titanium and manganese can be determined in the phosphate, if worth while.

[4] In washing with hot water, the precipitated iron and aluminium phosphates are partly hydrolysed, with the production of a soluble acid phosphate and an insoluble basic phosphate. Hence, the composition of the precipitate is determined by the method used in washing, and accordingly, the actual composition of the precipitate must be established in work making a pretence to accuracy.

[5] A prolonged blasting—about 15 minutes—is necessary to get a constant weight.

[6] There is some danger of losing phosphoric oxide, if any be present, in evaporating the sulphuric acid to dryness, as described on page 607, and also during the pyrosulphate fusion —H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2.** 575, 1871.

[7] Under some conditions, when the weight is very small, it can be assumed that the precipitate is a mixture of $FePO_4$ and $AlPO_4$, and half the weight of the precipitate is taken to represent "$Fe_2O_3 + Al_2O_3$."

[8] If any flocculent matter should separate during the evaporation, it is filtered off, as indicated on page 218, and examined for magnesia.

The alkalies are determined on a separate sample. The results are good, but the washing of the precipitated calcium sulphate is very tedious, and, if the alcohol be not recovered, the expense is a serious item when many determinations are made. The following numbers represent three determinations with one (unfired) sample :

$Ca_3(PO_4)_2$	34·20	34·26	34·51	per cent.
$Al_2O_3 + Fe_2O_3$	12·32	12·29	12·17	per cent.

It is perhaps advisable to again emphasise the fact that the precipitated aluminium and iron phosphates are progressively hydrolysed[1] by a prolonged washing. Twenty washings with a 5 per cent. solution of ammonium nitrate gave a theoretical yield of aluminium phosphate, but fifty washings gave a slightly low result owing to the formation of a soluble phosphate and an insoluble basic phosphate. Experiments with known mixtures show that the method gives good results in the presence of calcium, magnesium, sodium, and potassium salts. If appreciable quantities of fluorides or sulphates be present, the results are poor, because the aluminium phosphate is imperfectly precipitated—page 180.

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[1] Cold or hot alkaline acetates also dissolve aluminium phosphate slowly.

CHAPTER XLII.

THE DETERMINATION OF SULPHUR.

> There is little chance of discovering any exact method for the determination of sulphates by precipitation as barium sulphate, which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisite conditions appear to be mutually incompatible.—J. Johnston and L. H. Adams.

§ 318. The Properties of Barium Sulphate.

Sulphur compounds in clays and silicates are transformed into soluble sulphates by fusion with sodium carbonate under oxidising conditions. The acidified solution is treated with a soluble barium salt, and insoluble barium sulphate is precipitated. This is washed, dried, ignited in the usual manner, and weighed as $BaSO_4$. Until comparatively recently, many books on analysis gave students the impression that the weight of the barium sulphate indicated the amount of sulphuric oxide in a given sample with unerring precision. It has long been certain that the results, unless definite precautions be taken, can only be approximately correct, and may indeed be untrustworthy. The method, in fact, is peculiarly sensitive to modifications in the conditions of the experiment. In 1871, Glover[1] quoted the following analyses of seven different samples of pyrites by three different professional analysts, A, B, C:—

Table LXX.—Test Analyses for Sulphur in Pyrites.

	Per cent. of sulphur.						
Sample No. .	1.	2.	3.	4.	5.	6.	7.
A . . .	38·80	40·90	39·60	39·30	41·60	38·20	39·70
B . . .	38·00	40·90	39·10	39·50	41·40	38·00	39·20
C . . .	40·20	42·70	41·10	40·70	43·50	40·00	41·10

In some cases the difference amounts to nearly 2 per cent. Since this sort of thing is not very different from what occurs even to-day, it is necessary to examine the more important sources of error.

It is generally stated that sulphuric acid will show one part of "barium" in between 80,000 and 250,000 parts of solution. According to Böttger,[2] 0·0000015 gram-molecules of potassium sulphate per litre will give a sensible turbidity with barium chloride in about 6 hours, and 0·0000039 gram-molecules of barium chloride per litre will give a sensible turbidity with potassium sulphate in about 2 hours.

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[1] J. Glover, *Chem. News*, 23. 57, 1871.

[2] F. Jackson, *Journ. Amer. Chem. Soc.*, 25. 992, 1903; W. Böttger, *Zeit. angew. Chem.*, 25. 1992, 1912.

1. *The Adsorption of Salts by the Precipitated Barium Sulphate.*—Turner[1] long ago pointed out that barium sulphate has a tendency to carry down other salts during its precipitation.

Turner said (1829): "The adhesion of potassium sulphate to the precipitate ensues even in a dilute solution; and it is not prevented by the presence of other salts, such as potassium nitrate, ammonium chloride, or ammonium nitrate. The quantity of adhering salt is variable, depending apparently as well on the relative quantity of the two salts, and the strength of the solution, as on the manner and extent of edulcoration. I have known it to increase the weight of the barium sulphate by 1 per cent."

A large number of observers[2] have placed similar facts on record. Salts of the alkalies and the alkaline earths,[3] silica, magnesium, cobalt, copper, iron,[4] and aluminium compounds,[5] etc., may be carried down[6] with the precipitate. In illustration, known quantities of barium chloride and sulphuric acid were mixed in the presence of the salts indicated in Table LXXI.; the results were somewhat high under conditions where slightly low results would have been obtained in the absence of the salts.

Table LXXI.—Effect of Foreign Salts on the Precipitation of Barium Sulphate.

$BaCl_2.2H_2O$, grm. taken.	Salt added, 5 grm.	$BaSO_4$ found.	Error.
0·5046	...	0·4814	−0·0004
0·5020	KCl	0·4931	+0·0137
0·5013	NaCl	0·4849	+0·0061
0·5027	$KClO_3$	0·4907	+0·0107

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[1] E. Turner, *Phil. Trans.*, **119**. 295, 1829; H. Rose, *Pogg. Ann.*, **113**. 627, 1861.

[2] R. Fresenius, *Zeit. anal. Chem.*, **8**. 52, 1869; **9**. 52, 1870; **19**. 53, 1880; **16**. 339, 1877; **30**. 452, 1891; R. Fresenius and E. Hintz, *ib.*, **35**. 170, 1896; G. Brügelmann. *ib.*, **16**. 19, 1877; E. Hintz and H. Weber, *ib.*, **45**. 31, 1906; H. Weber, *ib.*, **45**. 714, 1906; G. Lunge, *ib.*, **19**. 419, 1880; C. Meineke, *ib.*, **38**. 210, 1899; T. O. Sloane, *Journ. Amer. Chem. Soc.*, **3**. 37, 1881; O. W. Foulk, *ib.*, **18**. 793, 1896; J. Johnston and L. H. Adams, *ib.*, **33**. 829, 1911; L. Archbutt, *Journ. Soc. Chem. Ind.*, **9**. 25, 1890; W. Smith, *ib.*, **1**. 85, 1882; P. Jannasch, *Journ. prakt. Chem.* (2), **40**. 233, 1889; P. Jannasch and T. W. Richards, *ib.* (2), **39**. 321, 1889; A. Mitscherlich, *ib.* (1), **83**. 456, 1861; E. Siegle, *ib.* (1), **69**. 142, 1856; C. Diehl, *ib.* (1), **79**. 430, 1860; R. Silberberger, *Chem. Monats.*, **25**. 220, 1904; A. Ziegeler, *Chem. Centr.* (3), **12**. 555, 1881; W. Ostwald, *Zeit. phys. Chem.*, **34**. 495, 1900; G. Hulett, *ib.*, **37**. 385, 1901; **47**. 357, 1904; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, **19**. 97, 1899; **22**. 424, 1900; G. Hulett and L. H. Duschak, *ib.*, **40**. 196, 1904; O. N. Heidenreich, *ib.*, **20**. 233, 1899; A. Fischer, *ib.*, **42**. 408, 1904; A. Thiel, *ib.*, **36**. 85, 1903; T. W. Richards, *ib.*, **1**. 150, 187, 1892; *Proc. Amer. Acad.*, **26**. 258, 1891; T. W. Richards and H. G. Parker, *ib.*, **31**. 67, 1896; *Zeit. anorg. Chem.*, **8**. 413, 1895; O. Herting, *Zeit. angew. Chem.*, **12**. 274, 1899; O. Herting, *Chem. Ztg.*, **23**. 768, 1899; E. Ruppin, *ib.*, **33**. 17, 398, 1909; **34**. 1201, 1910; J. F. Sacher, *ib.*, **33**. 28, 1909; O. Folin, *Journ. Biol. Chem.*, **1**. 131, 1905; E. F. Teschemacher and J. D. Smith, *Chem. News*, **24**. 61, 66, 171, 1871; N. Glendinning and A. Edgar, *ib.*, **24**. 140, 220, 1871; S. Wyrouboff, *Bull. Soc. Chim.* (3), **21**. 1046, 1899; J. I. Phinney, *Amer. J. Science* (3), **45**. 468, 1891; W. S. Allen and H. B. Bishop, *Internat. Cong. App. Chem.*, **8**. i, 33, 1912.

[3] According to F. Stolba (*Dingler's Journ.*, **168**. 43, 1863), potassium sulphate is more easily removed by washing than sodium sulphate.

[4] According to C. R. Gyzander (*Chem. News*, **93**. 213, 1906), ferrous salts are not so liable to contaminate the precipitated barium sulphate as ferric salts; hence, before precipitating the barium salt in the presence of iron, some recommend the addition of a reducing agent such as sodium thiosulphate or hydroxylamine hydrochloride.

[5] E. A. Schneider, *Zeit. phys. Chem.*, **10**. 425, 1895; H. J. M. Creighton, *Zeit. anorg. Chem.*, **63**. 53, 1909.

[6] Either by adsorption, or mechanically.

Hence, some of the salt carried down with the precipitate is probably weighed with the barium sulphate.[1] Further experiments show that occlusion occurs in presence of all the common metallic salts, and of sulphates soluble in water; and that the amount of this occlusion per gram-molecule is nearly the same for all the metals. Hence, *all barium sulphate precipitates have a complex composition owing to the presence of occluded salts*—sodium nitrate,[2] ammonium salts, sodium, potassium, and ammonium chlorides, potassium and sodium sulphates, etc. Potassium salts are more likely to be occluded than sodium salts. Magnesium sulphate is scarcely occluded at all, and the error from alkaline and ammonium chlorides is very small, unless very small precipitates are in question, when this error becomes of increasing importance. In general, *the greater the concentration of the alkaline salts in the mother liquid, the greater the amount of salt occluded by the precipitate.* For instance, Johnston and Adams find that 350 c.c. of a solution containing the equivalent of 2 grms. of barium sulphate, 2 c.c. of a 2 per cent. solution of hydrochloric acid, and

Sodium chloride	0	5	10	20	30	50	70	100	grms.
Occluded salt in precipitate .	8·2	17·4	19·0	24·4	31·4	38·4	47·6	45·8	mgrms.

Barium chloride, the precipitating agent, may also be carried down with the precipitated barium sulphate—about 0·15 per cent. is present in slowly formed precipitates.[3] Some of this may be removed by washing with dilute nitric or acetic acid, but another source of error may affect the work when the precipitate is subjected to acid treatment—page 614.

It is not always practicable to dissolve the precipitated barium sulphate and reprecipitate, as is frequently possible with most precipitates affected in a similar way. Mitscherlich[4] suggested purifying the precipitate by dissolving it in concentrated sulphuric acid,[5] and reprecipitating the barium sulphate by dilution with water. This process is by no means satisfactory, and Mar[6] obtained better results by evaporating the sulphuric acid solution of the sulphate to dryness, and washing the crystals so obtained on an asbestos pad in a Gooch's crucible with water. Ignite and weigh. The removal of silica by digesting the barium sulphate with hydrofluoric acid requires care, because barium sulphate is decomposed by the treatment. Thus Sleeper[7] obtained the following numbers on weighing 2·1563 grms. of barium sulphate after each successive evaporation with hydrofluoric acid:

2·1457 2·1295 2·1224 2·1041 2·1022 2·0800 2·0549

The barium sulphate, after the digestion, should be treated with a drop of sulphuric acid. As a matter of fact, Sleeper observed no contamination of the precipitated barium sulphate with silica when the former was precipitated from artificial mixtures of a soluble sulphate with sodium silicate.

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[1] Y. Kato and I. Noda, *Mem. Coll. Sci. Eng. Kyōtō*, **2.** 217, 1910; E. T. Allen and J. Johnston, *Journ. Amer. Chem. Soc.*, **32.** 588, 1910; *Journ. Ind. Eng. Chem.*, **2.** 196, 1910.

[2] This forms caustic soda on ignition.

[3] A. Mitscherlich, *Pogg. Ann.*, **55.** 214, 1842; E. Siegle, *Journ. prakt. Chem.* (1), **69.** 142, 1856.

[4] A. Mitscherlich, *Journ. prakt. Chem.* (1), **83.** 456, 1861; W. G. Mixter, *Chem. News*, **27.** 53, 1873; *Amer. J. Science* (3), **4.** 90, 1872; F. H. Storer and A. H. Pearson, *ib.* (2), **48.** 870, 1869. F. Stolba (*Dingler's Journ.*, **186.** 43, 1863; *Chem. News*, **9.** 133, 1864) proposes to purify the barium sulphate by washing it with a solution of copper acetate followed by hot water.

[5] J. Nickles, *Amer. J. Science* (2), **39.** 90, 1865; *Chem. News*, **11.** 125, 1865.

[6] F. W. Mar, *Chem. News*, **63.** 256, 1891; *Amer. J. Science* (3), **43.** 525, 1890.

[7] J. F. Sleeper, *Chem. News*, **69.** 63, 1894.

The adsorbed salts are sometimes removed by dissolving the precipitate[1] in a platinum crucible or dish with 10–15 c.c. of concentrated sulphuric acid, and pouring the solution, in a thin stream, with vigorous stirring, into 350 c.c. of water. The solution is heated to facilitate the filtering of the purified barium sulphate. The soluble salts to a great extent remain in solution. Examples of two successive extractions of two different precipitates may be quoted:

	I.	II.	
First extraction	0·0101	0·0248	grm. sodium sulphate.
Second extraction	0·0008	0·0021	grm. sodium sulphate.

The important thing is to avoid the mutual precipitation of salts from the mother liquid with the barium sulphate. The barium chloride solution should not be added suddenly, but rather in drops, gradually, with constant stirring. In illustration, the two following experiments may be cited to show the difference in the weight of the precipitate obtained when the barium chloride is added suddenly and in drops—the theoretical amount of barium sulphate was 49·33 per cent.:

	I.	II.
In drops	49·23	49·30
Suddenly	50·03	49·90

These and other experiments show that *the rapid addition of the precipitant gives a more impure precipitate than when the precipitant is added slowly.* Indeed, if the precipitate which has been formed suddenly be fused with sodium carbonate, and, when cold, leached with water, and the clear solution of the cake be treated with silver nitrate as described on page 652, a precipitate of silver chloride is obtained corresponding, in amount, with the excess in the preceding table, calculated on the assumption that the excessive amount of barium sulphate is due to adsorbed barium chloride. This demonstrates the adsorption of barium chloride by the precipitate formed under the conditions stated—see page 72.

If much hydrochloric acid be also present, it requires a greater excess of barium chloride to precipitate a given amount of sulphuric acid; and conversely,[2] a greater excess of a soluble sulphate is required to precipitate a given amount of barium chloride. Hence, *the risk of contamination of the precipitated sulphate with barium chloride is greater, the greater the amount of free hydrochloric acid present*;[3] *but, within certain limits, the greater the acidity of the solution, the less the amount of salt occluded by the precipitated barium sulphate.* Allen and Johnston consider that the best results are obtained when the "sulphate" solution contains 20 to 30 c.c. of 5N-hydrochloric acid per 500 c.c.,[4] and the amount of "sulphuric acid" is such that 5 to 10 c.c. of normal barium chloride solution are needed for the precipitation. If barium is to be determined, the solution should contain about 0·5 per cent. hydrochloric acid before adding the precipitating agent, say ammonium sulphate (10 per cent. solution). A considerable excess of the latter is needed for complete precipitation.

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[1] E. Ruppin (*Chem. Ztg.*, 33. 17, 398, 1908; 34. 1201, 1910) boils the precipitate four times in acidulated water. J. F. Sacher, *ib.*, 33. 218, 941, 1909; M. J. van't Kruys, *Chem. Weekblad*, 6. 735, 1909.

[2] F. W. Mar (*Chem. News*, 63. 256, 1891; *Amer. J. Science* (3), 41. 288, 1891; (3), 43. 525, 1890) and P. E. Browning (*ib.* (3), 45. 399, 1893) state that if a sufficient excess of sulphuric acid be present, the precipitation of barium as sulphate is not affected by the presence of up to 10 per cent. by volume of hydrochloric acid, nitric acid, or aqua regia. E. Murmann (*Oester. Chem. Ztg.*, 13. 227, 1910) recommends a large excess of hydrochloric acid with a few drops of alcohol to facilitate the precipitation of the barium sulphate.

[3] J. O. Roos, *Kungl. Teknis. Högs. Materialpruf.*, 34, 1896–1906; M. Huybrechts, *Bull. Soc. Chim. Belg.*, 24. 177, 281, 1910.

[4] O. Folin (*Journ. Biochem.*, 1. 131, 1906) prescribes, as safe limits, 1 to 4 c.c. of concentrated hydrochloric acid per 150 c.c. of solution, that is, 4·5 to 18·5 c.c. of 20 per cent. acid per 350 c.c.

2. *The Solubility of Barium Sulphate.*—Barium sulphate is but sparingly soluble in water,[1] since 100 c.c. of water at 10° dissolve 0·000197 grm. of barium sulphate, while 100 c.c. of water at 100° dissolve 0·00031 grm. The freshly precipitated sulphate is rather more soluble than the precipitate which has stood for some time in contact with the mother liquid.[2] Curiously enough, *a precipitate of barium sulphate which has been filtered and washed immediately after precipitation is less easily freed from occluded salts by washing, and therefore contains more occluded salts than one which has been left to stand some time,* say overnight. The difference is considerable when the amount of the salt in the solution is large. For instance, a solution containing the equivalent of 2 grms. of barium sulphate and 5 grms. of sodium sulphate furnished a precipitate containing:

Occluded Na_2SO_4 .	22·6	19·0	17·4	14·0	12·2	10·4	8·2	7·6 mgrms.
Time standing .	15 min.	3 hrs.	18 hrs.	2 days	4 days	48 days	150 days	210 days.

These experiments were made at 20°. Experiments at 100° showed that rather less salt is occluded than at the lower temperature.

The solubility of the barium sulphate is augmented by acids.[3] Thus, 100 c.c. of a solution containing hydrochloric acid dissolved the following amounts of barium sulphate:

HCl	1·82	3·65	7·29	grms.
$BaSO_4$	0·0067	0·0089	0·0101	grm.

and nitric acid:

HNO_3 . . .	3·15	6·31	12·61	31·52	grms.
$BaSO_4$ . . .	0·0070	0·0107	0·0170	0·0241	grm.

Dilute sulphuric acid lowers the solubility, but barium sulphate is fairly soluble in the concentrated acid. Thus, 100 parts of sulphuric acid, sp. gr. 1·32, dissolve 5·69 parts of barium sulphate, and 100 parts of sulphuric acid, sp. gr. 1·9, dissolve 15·89 parts.[4] Again, 100 c.c. of 40 per cent. hydrobromic acid dissolve 0·04 grm. of barium sulphate; and the same amount of 40 per cent, hydriodic acid 0·0016 grm.[5] Hydrogen peroxide[6] and free chlorine[7] also increase the solubility of barium sulphate.

The increased solubility of barium sulphate in the more concentrated acids shows that if, say, hydrochloric acid be present in great excess, the solution should be partly neutralised before the precipitation is made. Alkaline chlorides, barium nitrate, and potassium chlorate do not appreciably affect the solubility of barium sulphate; but alkaline nitrates,[8] phosphates,[9] and salts of the organic acids,[10] have a marked effect on the solubility.

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[1] F. C. Calvert, *Chem. Gaz.*, **13**. 55, 1856; A. F. Holleman, *Zeit. phys. Chem.*, **12**. 125, 1893; F. Kohlrausch and F. Rose, *ib.*, **12**. 234, 1893; F. Kohlrausch, *ib.*, **50**. 355, 1905.

[2] Page 212. W. H. Wollaston, *Phil. Trans.*, **103**. 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, **34**. 495, 1900; G. Hulett, *ib.*, **37**. 385, 1901; **47**. 357, 1904.

[3] G. S. Fraps, *Amer. Chem. Journ.*, **27**. 283, 1902; H. Rose, *Pogg. Ann.*, **95**. 108, 1855; R. Piria, *Il Cimento*, **5**. 257, 1847; E. Siegle, *Journ. prakt. Chem.* (1), **69**. 142, 1856; E. C Nicholson and D. S. Price, *Phil. Mag.* (4), **11**. 169, 1856; H. M. Noad, *Journ. Chem. Soc.*, **9**. 15, 1856; W. Ostwald and W. Banthisch, *Journ. prakt. Chem.* (2), **29**. 52, 1884; C. Gutkowsky, *Ber.*, **5**. 330, 1872.

[4] H. Struve, *Zeit. anal. Chem.*, **9**. 34, 1870; C. C. Selleck, *Pogg. Ann.*, **133**. 137, 1868.

[5] A. R. Haslam, *Chem. News*, **53**. 87, 1886.

[6] A. Gawalovski, *Zeit. Oester. Apoth. Ver.*, **44**. 258, 1900.

[7] O. L. Erdmann, *Journ. prakt. Chem.* (1), **75**. 214, 1858.

[8] M. Mittentzwey, *Journ. prakt. Chem.* (1), **75**. 214, 1858; R. Fresenius, *Zeit. anal. Chem.*, **9**. 62, 1870; J. J. Berzelius, *Ann. Chim. Phys.*, **14**. 374, 1820.

[9] Some barium phosphate is formed, and so remains in solution. T. Scheerer, *Journ. prakt. Chem.* (1), **75**. 113, 1858.

[10] For example, alkaline citrates. J. Spiller, *Journ. Chem. Soc.*, **10**. 110, 1858; *Chem. News*, 8. 280, 1863; **19**. 166, 1869.

The solubility of the precipitate is increased by the presence of thorium, ferric, and aluminium salts, but not so much by magnesium salts. Thus,

Grams per litre . . .	1	2·5	5	10	25	50	100
	Grams of barium sulphate dissolved per 100 c.c.						
Ferric chloride . . .	0·0058	0·0072	0·0115	0·0123	0·0150	0·0160	0·0170
Aluminium chloride . .	0·0033	0·0043	0·0060	0·0094	0·0116	0·0170	0·0175
Magnesium chloride . .	0·0030	0·0030	0·0033	0·0033	0·0050	0·0050	0·0050

Jannasch and Richards[1] attributed this effect to the formation of a double ferric barium sulphate, and add that, in a solution containing ferric chloride, "an accurate determination of sulphuric acid by direct precipitation with barium chloride is not practicable." Hence, in determining sulphur in pyrites, etc., the iron should be first removed, as Lunge recommends, by precipitation with ammonia before precipitating the barium sulphate.[2] An insignificant trace of sulphur may be lost owing to adsorption by the ammonia precipitate, or by the separation of a basic ferric sulphate with the ammonia precipitate. According to Lunge,[3] this need not be feared if the solution, after treatment with a moderate excess of ammonia, be heated to about 60° or 70° (not over) for about 10 minutes. The solution should still smell strongly of ammonia. The precipitate is filtered off, and the sulphate precipitated from the filtrate as described below. With the same object in view, Treadwell[4] recommends supersaturating the solution with ammonia in the cold, and afterwards raising the temperature almost to boiling with constant stirring. The precipitate is filtered and washed until the washings give no turbidity with barium chloride after standing 5 minutes.[5]

The presence of copper nitrate, too, gives low results owing to the solubility of barium sulphate in an aqueous solution of copper nitrate. Hence, adds Phillips,[6] the nitric acid should be replaced by hydrochloric acid by converting the copper nitrate to chloride. The same difficulty does not then occur.

3. *The Reduction of the Sulphate to Sulphide.*—When barium sulphate is ignited in the presence of filter paper, organic matter, etc., "an appreciable amount of barium sulphate may be reduced to sulphide, and the amount so reduced may be twice as great in a covered crucible as when ignited in an open crucible. The precipitate should be moistened with sulphuric acid, and again ignited in order to transform the sulphide back to sulphate.[7] If a Gooch's crucible be employed, Ripper[8] says that the results are inaccurate, because the adhesion of the barium sulphate to the asbestos prevents the proper washing of the precipitate. This

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[1] G. S. Fraps, *Amer. Chem. Journ.*, **27**. 288, 1902; R. Fresenius, *Zeit. anal. Chem.*, **9**. 62, 1870; P. Jannasch and T. W. Richards, *Journ. prakt. Chem.* (2), **39**. 321, 1889; **40**. 233, 1889.

[2] M. Dennstedt and F. Hassler, *Zeit. angew. Chem.*, **16**. 1233, 1903; G. Lunge and R. Stierlin, *ib.*, **18**. 446, 1656, 1921, 1905; G. Lunge, *ib.* **16**. 1081, 1903; *Zeit. anal. Chem.*, **19**. 414, 1880; *Journ. Amer. Chem. Soc.*, **17**. 69, 1895; T. S. Gladding, *ib.*, **16**. 398, 1894; **18**. 446, 1896; N. J. Lane, *ib.*, **18**. 682, 1896; G. von Knorre, *Chem. Ind.*, **28**. 2, 1906; K. Jene, *Chem. Ztg.*, **29**. 362, 1905; H. Mennicke, *ib.*, **29**. 4951, 1905; B. N. Gottlieb, *ib.*, **29**. 668, 1905.

[3] G. Lunge, *Zeit. anorg. Chem.*, **19**. 454, 1899; F. W. Küster and A. Thiel, *ib.*, **19**. 97, 1899; **22**. 424, 1900; O. Herting, *Zeit. angew. Chem.*, **12**. 274, 1899; O. Herting, *Chem. Ztg.*, **23**. 768, 1899; O. N. Heidenreich, *Zeit. anorg. Chem.*, **20**. 233, 1900; C. R. Gyzander, *Chem. News*, **93**. 213, 1906.

[4] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**. 385, 1911.

[5] In doubtful cases the precipitate should be ignited and fused with sodium carbonate, and the aqueous extract of the mass tested to make sure that sulphates are absent.

[6] H. J. Phillips, *Chem. News*, **62**. 239, 1890. For thorium, see E. White, *Thorium and its Compounds*, London, 26, 1912.

[7] C. W. Marsh, *Journ. Anal. App. Chem.*, **3**. 164, 1889; *Chem. News*, **59**. 309, 1889; S. F. Acree, *Journ. Biol. Chem.*, **2**. 135, 1906; H. Pellet, *Ann. Chim. Anal.*, **12**. 186, 318, 1907; P. Truchot, *ib.*, **12**. 267, 1907.

[8] M. Ripper, *Zeit. anorg. Chem.*, **2**. 36, 1892; F. W. Mar, *Chem. News*, **63**. 256, 1891; *Amer. J. Science* (3), **43**. 525, 1890; J. J. Phinney, *ib.* (3), **45**. 468, 1891.

statement is opposed to the work of Mar and Phinney, who recommend the use of Gooch's crucible. With care, the Gooch's crucible does not furnish results less accurate than filter paper.

4. *Losses by Volatilisation.*—Barium sulphate is not appreciably decomposed at temperatures likely to be obtained during the ignition over a blast gas flame. Doeltz and Mostowitsch[1] found that a sample of pure barium sulphate lost 9 per cent. in weight when heated between 10 and 20 minutes in a platinum crucible at 1580°. This temperature is, however, much higher than is obtained in ordinary blasting, and if barium sulphate should be so decomposed, the original amount of barium sulphate can be restored by moistening with sulphuric acid and recalcination for a short time. If, however, much silica be present, appreciable decomposition may occur at much lower temperatures. Allen and Johnston[2] say that, if the barium sulphate be precipitated from solutions containing alkali sulphates, it "always occludes a certain amount of 'free' sulphuric acid which is taken up as acid sulphate of the alkali metal." Alkaline chlorides increase the amount of this impurity, and it is greater with solutions containing potassium than sodium sulphate. The "free" sulphuric acid[3] is lost by volatilisation during ignition, whereas under ideal conditions all the sulphuric acid should have been converted into barium sulphate (in the determination of sulphur). If ammonium salts are present, some ammonium sulphate is precipitated with the barium sulphate; and since all but a trace of the occluded ammonium sulphate is driven off during ignition, the total loss by volatilisation is the resultant of these two effects. For instance, by adding ammonium sulphate to 350 c.c. of a solution containing 20 per cent. of hydrochloric acid and the equivalent of 2 grms. of barium sulphate, it was found that with:

Table LXXII.—Volatilisation Losses during Ignition of Barium Sulphate.

Ammonium chloride.	Loss in grms.		
	Due to ammonium sulphate.	Due to "free" sulphuric acid.	Total.
grm.			
0	...	...	0·0112
0	...	...	0·0111
5	0·0244	0·0039	0·0283
5	0·0244	0·0055	0·0299
10	0·0259	0·0113	0·0372
10	0·0259	0·0096	0·0355

Hence, ammonium salts and a large excess of free acid should be avoided in solutions where the sulphur is to be determined.

5. *Sulphur in the Glass of Beakers and Flasks.*—According to Bunge,[4] baryta water and lime water can act on glass, and a thin layer of barium sulphate is often deposited on glass in which such solutions have been used. Glass made from Glauber's salt (sodium sulphate), etc., usually contains sulphates. Hence the possibility of a slight error by the solvent action of reagents on the glass vessels employed in the work.

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[1] F. O. Doeltz and W. Mostowitsch, *Zeit. anorg. Chem.*, **54**. 146, 1907; W. Mostowitsch, *Metallurgie*, **6**. 450, 1909; W. Schütz, *ib.*, **8**. 228, 1910.

[2] E. T. Allen and J. Johnston, *Journ. Amer. Chem. Soc.*, **32**. 588, 1910; *Journ. Ind. Eng. Chem.*, **2**. 196, 1910.

[3] It arises from the free acid in the original solution, and increases with it up to a certain point.

[4] C. Bunge, *Zeit. anal. Chem.*, **52**. 15, 1913.

§ 319. The Determination of Sulphates in Clays and Insoluble Silicates.

The Fusion.—It is first necessary to get the silicate into solution. A gram of the dry material[1] is fused in a platinum crucible with five to six times its weight of sodium carbonate. If iron pyrites be present, about 0·25 grm. of sodium nitrite[2] should also be intimately mixed with the contents of the crucible. The mixture is heated very slowly, as described for the potassium pyrosulphate fusion (page 185).

Preventing Contamination with Sulphur from Flame Gases.—In order to protect the contents of the crucible from sulphur compounds derived from the flame gases, etc., Hillebrand[3] fits the crucible into a hole in an asbestos board; and Cumming, into a vitreous "quartz plate." The hole should be large enough to expose from one-half to two-thirds of the crucible to the flame. The asbestos will not stand the temperature many times, and if this material be used it is preferable to employ a disc of stiff platinum foil with a hole in the centre in conjunction with the asbestos board. The whole should be inclined at an angle, as illustrated in fig. 190, so as to deflect the products of combustion to the side, and prevent their coming in contact with the mouth of the crucible.[4]

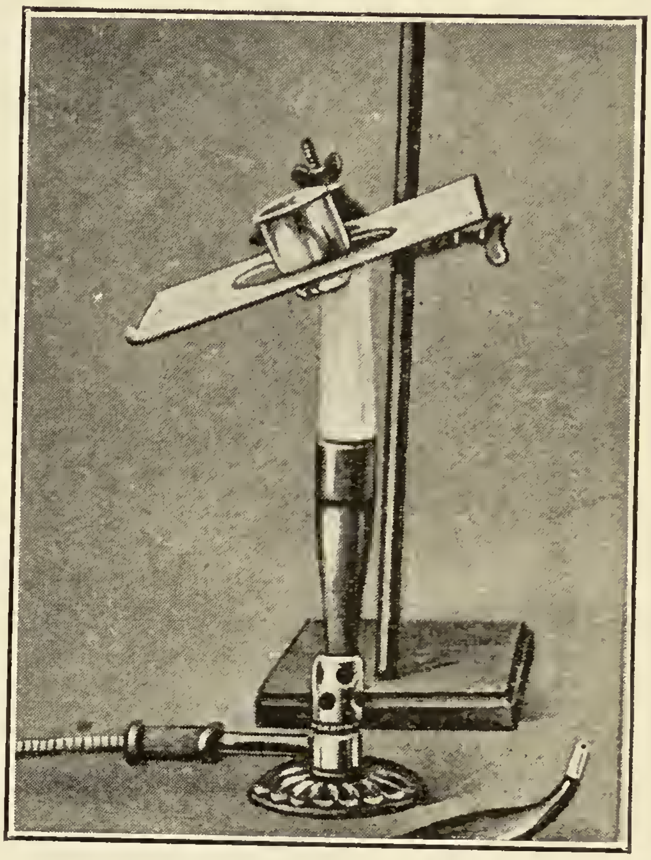

Fig. 190.—Fusion for sulphur.

One of the many forms of blast lamp on the market burning methylated spirit may be used with advantage for the fusion. There is then no need to protect the crucible as just described. Barthel's[5] lamps are quite satisfactory. Fig. 191 illustrates one in use. These lamps may be obtained equivalent to one, two, or four Bunsen's burners. Electric crucible furnaces can also be used.

The Leaching of the Fused Cake.—When the fusion is completed, and the crucible has cooled, the cake must be removed as described on page 165. The cake is taken up with water, not acid. Filter through a small filter paper, say

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[1] If sulphur, chlorine, and fluorine are to be determined, take 2 grms.

[2] Both nitrite and carbonate, and indeed all the reagents, should be tested to ensure the absence of sulphur compounds (page 461).

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **176**. 196, 1900; A. C. Cumming, *Proc. Roy. Soc. Edin.*, **32**. 17, 1912. The hole in the quartz plate can be bored on a lathe with a copper tube fed with carborundum.

[4] Contamination with Sulphur during Ignition over Gas Flames.—See D. S. Price, *Journ. Chem. Soc.*, **17**. 51, 1864; G. L. Ulex, *Deut. Ind. Ztg.*, **379**. 1870; *Zeit. anal. Chem.*, **10**. 246, 1871; J. W. Gunning, *ib.*, **7**. 480, 1868; U. Collan, *ib.*, **32**. 213, 1893; L. von Szathmary, *ib.*, **45**. 600, 1906; R. Fresenius, *ib.*, **16**. 339, 1877; Wagner, *ib.*, **20**. 323, 1881; A. Lieben, *ib.*, **32**. 214, 1893; *Monit. Scient.* (4), **6**. 683, 1892; A. Vogel, *Ber.*, **2**. 741, 1869; E. Privozink, *ib.*, **25**. 2200, 1886; G. Lunge, *Journ. prakt. Chem.* (2), **40**. 239, 1889; J. van Leeuwen, *Rec. Travs. Pays Bas*, **11**. 103, 1892; J. W. Gunning, *Chem. News*, **17**. 161, 1868; R. Woy, *Zeit. öffent. Chem.*, **8**. 389, 1902.

Contamination with Sulphur during Evaporation over Gas Flames.—See O. Binder, *Chem. Ztg.*, **16**. 254, 1892; E. von Meyer, *Journ. prakt. Chem.* (2), **42**. 267, 1892. On evaporating 2 litres of distilled water down to 50 c.c. in 6 hours on a water bath, Meyer found the water contaminated with sulphur equivalent to 0·0426 grm. of barium sulphate.

[5] G. Barthel, *Chem. Ztg.*, **16**. 1106, 1892; *Zeit. anal. Chem.*, **30**. 596, 1891; **31**. 67, 1892. Directions for use are supplied with the burner.

9 cm., and wash with a dilute solution of sodium carbonate. If chromium be present, the solution will be yellowish. The filtrate contains the alkaline sulphates, chlorides, and silicates; and the sodium salts of chromic, vanadic, phosphoric, arsenic, molybdic, and tungstic acids (if present). The barium carbonate and sodium zirconate, thoria, etc., if present, remain undissolved on the filter paper.[1] The filtrate is treated with barium chloride as described below.

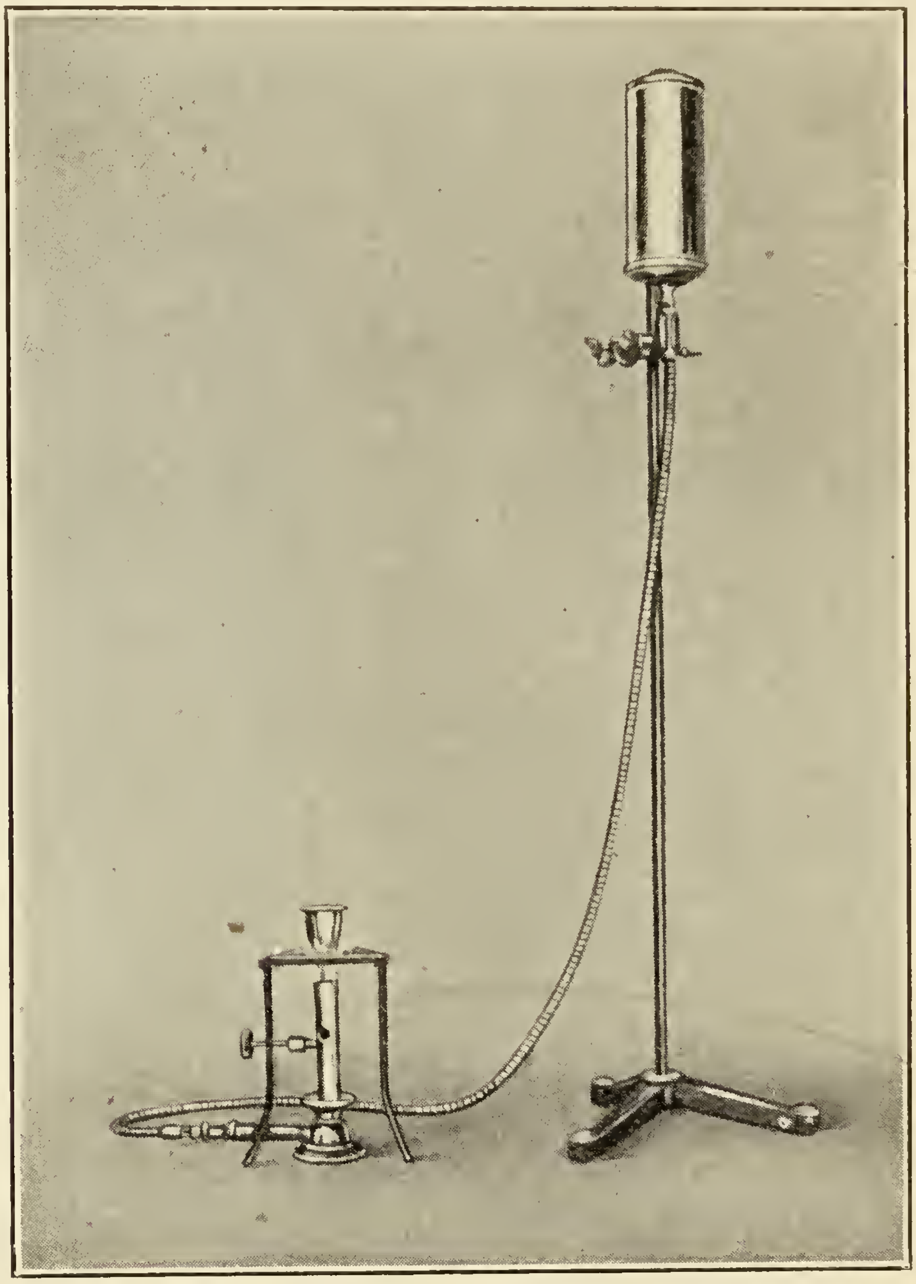

Fig. 191.—Spirit burner for sulphur fusions.

§ 320. The Determination of Sulphur as Barium Sulphate.

The solution[2]—150–250 c.c.—is acidified in a 500-c.c. beaker with about 5–10 c.c. of concentrated hydrochloric acid[3] and covered to prevent loss by spurting. Boil to expel carbon dioxide. If the solution be still alkaline, add more hydrochloric acid, but avoid a great excess. Wash down the sides of the beaker and the cover. The solution should be *slightly* acid, for the subsequent precipitation of the barium sulphate is not so complete if much hydrochloric acid be present,[4] although a large excess of hydrochloric acid gives a precipitate comparatively easy to filter. Heat the solution to boiling, and add, gradually,[1] with constant stirring, say, 15 or 25 c.c. of a hot aqueous solution of barium chloride,[2] but avoid a great excess.[3] Boil for a few minutes.[4] If a drop of the supernatant liquid on a watch-glass gives a turbidity with a drop of barium chloride, add sufficient barium chloride, slowly, drop by drop, with constant stirring, to precipitate all the sulphates in solution.[5] If no turbidity occurs, let the solution stand 2 hours in a warm place, or, say, overnight.[6] Carefully decant the clear through a (say, 7·5 cm.) filter paper, and wash four times by decantation with hot water,[7] containing 1 cubic centimetre of hydrochloric acid per litre.[8] Transfer the precipitate to the filter paper and wash with hot water until a drop of the filtrate gives no turbidity with silver nitrate. The washing of the barium sulphate requires great care, because other salts are precipitated from the solution along with the barium sulphate. Ignite the wet precipitate in a platinum crucible. The paper is folded loosely over the precipitate to prevent spattering. The paper should be smoked very gradually, and the final temperature should not exceed dull redness. The crucible is then cooled and weighed. Evaporate with a few drops of hydrofluoric acid and a drop of sulphuric acid to expel any silica present.[9] Re-ignite in an inclined, uncovered crucible over the Bunsen flame.[10] Any sulphides formed through the reducing action of the carbon of the filter paper are soon re-oxidised, and there is usually no need to add a drop of nitric acid and of sulphuric acid. If the washing has been properly done, the ignited barium sulphate will be a granular white powder; if otherwise, the powder may sinter to a more or less hard cake. The weight of the barium sulphate, multiplied by 0·13738, gives the corresponding amount of sulphur; the weight of the barium sulphate, multiplied by 0·3430, gives the corresponding amount of SO_3; and multiplied by 0·586, the corresponding amount of calcium sulphate; or Table XCII. may be used.

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[1] For the subsequent treatment of the residue, see page 498. There is reason to suppose that a little sulphur sometimes remains behind with the residue—*e.g.*, with thoria—because in test experiments less sulphur is found than is known to be present—E. White, *Thorium and its Compounds*, London, 26, 1912.

[2] If chlorine is to be determined, make the solution up to, say, 200 c.c., and set 100 c.c. aside for the chlorine determination (page 652). The volume of the solution should be such that a gram of barium sulphate is precipitated from 150 c.c. of mother liquid.

[3] The solution should contain 10 c.c. of concentrated hydrochloric acid per 150 c.c. of solution.

[4] The solution should also be free from nitrates and nitric acid for the best results.

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[1] Added from a burette or pipette with a capillary tip, so that about 4 minutes is needed for running in 20 c.c.

[2] BARIUM CHLORIDE SOLUTION.—Dissolve 122·16 grms. of barium chloride ($BaCl_2 . 2H_2O$) in 1000 c.c. of water (E). Here 1 c.c. corresponds with 0·104 grm. of $BaCl_2$. Note that commercial barium chloride sometimes contains sulphur compounds derived from the heavy spar used in making the chloride. The heavy spar is reduced to sulphide, and some soluble unoxidised sulphur compound may be retained by the crystals of the chloride—J. Pattinson and J. T. Dunn, *Journ. Soc. Chem. Ind.*, 24. 10, 1905. Note also that rubber stoppers sometimes contaminate solutions with sulphur compounds derived from the vulcanising agent—antimony sulphide. It may also be added that barium chloride prepared as a by-product in the manufacture of hydrogen peroxide may contain an impurity which reduces potassium permanganate—L. Blum, *Zeit. anal. Chem.*, 29. 139, 1890.

[3] This plan is of very great importance when a lot of sulphate is to be precipitated. The object is to prevent, as far as possible, the mechanical inclusion of barium chloride with the precipitate.

[4] When the precipitation occurs at the boiling temperature—both solutions hot—the precipitate is more granular, settles more quickly, filters better, and washes easier than if the solutions be cold (page 96).

[5] J. Johnston and L. H. Adams (*Journ. Amer. Chem. Soc*, 33. 829, 1911) recommend evaporation of the whole to dryness on a steam bath immediately after the precipitation; extract the mass with hot water; filter through paper; wash until the washings are free from chlorides; ignite very carefully over a Bunsen's burner to avoid reduction; etc. The weight of the precipitate is corrected by dissolving an equivalent amount of pure potassium or sodium sulphate in a medium resembling the solution to be analysed; and the sulphate determined as just indicated. The difference between the calculated and found results is used as a correction factor for the weight of the precipitate obtained in the actual analysis. In that case it is supposed that results can be obtained within ±0·05 per cent. of the total sulphur actually present in the solution.

[6] If a small amount of sulphur be present, the precipitate forms very slowly.

[7] Another beaker may be used for collecting the washings, to prevent having to re-filter *all* the liquid should the washings commence to run through turbid.

[8] It is well to test the runnings with a drop or two of sulphuric acid to make sure the barium chloride was in excess.

[9] If no silica is likely to be present, the ignition is conducted in a porcelain crucible.

[10] Not the blast, or SO_3 may be lost—C. W. Marsh, *Journ. Anal. App. Chem.*, 3. 164, 1889.

To illustrate the results which can be expected by this process, the following numbers represent the amounts of barium sulphate obtained in eight determinations with one-gram samples of the same clay:

0·0191; 0·0203; 0·0201; 0·0195; 0·0190; 0·0193; 0·0195; 0·0196.

The mean is 0·0196; the maximum deviation, ± 0·0007 grm.—that is, ± 0·07 per cent. on the total clay.

§ 321. The Filtration of the Barium Sulphate Precipitate.

Barium sulphate is a troublesome precipitate to filter, on account of its tendency to pass through the filter paper. A close-texture paper should therefore be used.[1] If the precipitate should run through the filter paper, refiltration is necessary. Some use a double filter paper—the two papers are folded separately, and one is placed inside the other; others use a Gooch's crucible packed with ignited asbestos[2]—this, however, does not allow the barium sulphate to be subsequently purified from silica. Another objection to Gooch's crucible turns on the fact that precipitates formed in feebly acid solutions are voluminous and inclined to clog the asbestos filter. Gooch's crucible is well adapted for small precipitates. Munroe's crucibles are good.

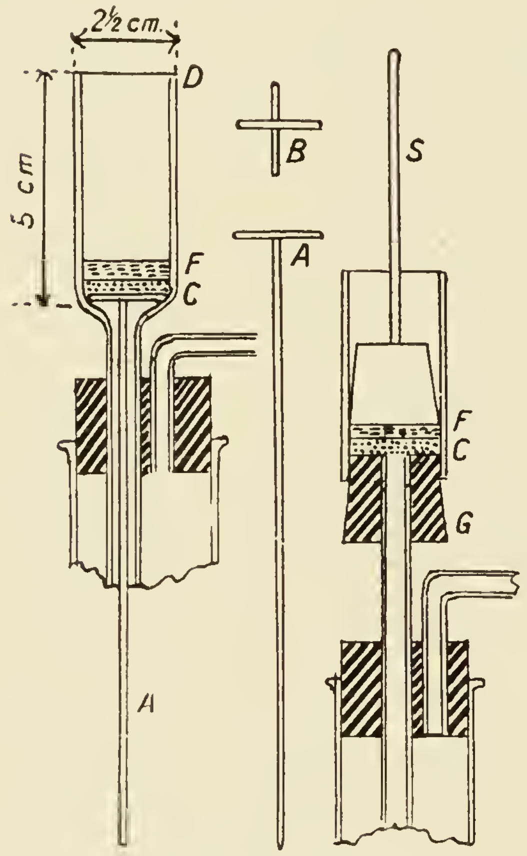

Fig. 192.—Shimer's filtration tubes.

P. W. Shimer[3] recommends a filter tube fitted to a filtration flask, as indicated in fig. 192. The wide part of filter tube *D* must be of uniform bore—about 2·5 cm. diameter, and 5 cm. long. The free end, *D*, is ground smooth, not melted smooth in the flame. *A* is a glass rod with a cross, *B*, at one end for supporting a disc of piano felt, *C*, approximately 0·75 cm. thick. The felt is cut by means of a cork-borer or wad-cutter very slightly larger than the bore of the filter tube. Fit the tube in a filter flask and apply gentle suction. Pour some filter-paper pulp (page 179) on to the felt to make a bed, *F*, about 0·6 cm. thick. Compact the pulp by the aid of a "stamper," *S*, made by fitting a glass rod into a hole bored half way through a rubber stopper at the narrow end. Wash the filter two or three times with water. Now run the contents of the beaker containing the barium sulphate precipitate through the filter tube and wash as usual. Then, by means of the glass rod *A*, push the felt out of the tube, so that felt and pulp, etc., are transferred to a weighed crucible. Remove the felt by means of a pair of forceps, and ignite the contents of the crucible in the usual manner. Any precipitate sticking to the sides of the tube is carried forward with the pulp. It is therefore important to select a filter tube with uniform sides. The tube on the right of fig. 192 represents a tube rather more easily made than that just described. It requires very little additional description. The rubber stopper *G* is of such a size that it can be easily pushed up the cylinder *D*.

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[1] Say, M. Dreverhoff's No. 311 or 400; or C. Schleicher and Schüll's No. 589, blue band.

[2] L. L. de Koninck, *Lehrbuch der chemischen Analyse*, Berlin, **1**. 388, 1904. The use of organic substances (page 179)—starch paste, etc.—is inadvisable on account of their reducing action when the sulphate is ignited. H. N. Warren (*Chem. News*, **61**. 63, 1870) recommends the coagulation of the precipitate by the addition of a few drops of an ethereal solution of pyroxylin (page 180), but we have then to fight the tendency of the coagulating precipitate to mechanically enclose some mother liquid; J. B. Krak (*Chemist Analyst*, **5**. 26, 1912) removes supernatant liquid when the precipitate has settled, and agitates thoroughly with 10 c.c. of a slightly acid saturated solution of sodium acetate. This curdles the precipitate and enables it to be filtered by suction.

[3] P. W. Shimer, *Journ. Amer. Chem. Soc.*, **27**. 287, 1905; H. P. Mason, *Chem. News*, **91**. 180, 1904.

The results with this arrangement are a little high, owing to the difficulties in washing large precipitates on pulp and on asbestos filters. Such filters are very liable to clog. Porous earthenware and alundum ware crucibles have recently been recommended for the filtration. The crucibles are used as described, § 324, page 630. When certain filtrates have passed through porous earthenware or alundum cups, a loss of weight occurs owing to the solvent action of the solution. Hence, the use of the cups is somewhat risky if the possibility of this error be ignored.

§ 322. The Determination of Sulphur in Pyrites, Limestones, Coals, etc.

The sulphur question is of some importance in certain branches of the clay industries, not only on account of the defects produced in glazes by fuels with abnormal amounts of sulphur; but the manufacture of some modern steels is influenced by the sulphur in the bricks, derived (1) by absorption from the fuel gases, and (2) from the sulphates or pyrites in the clays themselves. The methods for the quantitative determination of sulphur in coal, clays, silicates, etc., may be conveniently grouped under four headings.[1] The selection of the process for any particular problem is to be decided by the number of determinations to be made, the object of the determinations, and the nature of the samples under investigation.

I. *Dry Fusion with Alkalies followed by Treatment with Oxidising Agents.*

Eschka's Method for Coal, Coke, etc.—This process[2] depends upon the oxidation of the sulphur of the fuel by the oxygen of the air in the presence of magnesia,[3] and sodium carbonate;[4] and on the transformation of the products of the oxidation into sulphates by boiling ammonium nitrate. Bromine water is now generally used for the oxidation. The sulphates are then precipitated by barium chloride in the usual manner. The results are good, and the process is in common use. Details of the operation are as follow:

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[1] L. Campredon, *Dosage du Soufre dans les produits de la Sidérugie*, Paris, 1896.

[2] A. Eschka, *Oester. Zeit. Berg. Hütt.*, **22**. 111, 1874; *Zeit. anal. Chem.*, **13**. 344, 1874; L. Blum, *ib.*, **27**. 445, 1888; O. Herting, *Chem. Ztg.*, **23**. 768, 1899; G. L Heath, *Journ. Amer. Chem. Soc.*, **20**. 630, 1898; **21**. 1127, 1899; S. S. Sadtler, *ib.*, **27**. 1188, 1905; F. U. R. Stehmann, *ib.*, **24**. 644, 1902; A. C. Langmuir, *ib.*, **22**. 99, 1900; C. W. Stoddart, *ib.*, **24**. 852, 1902; A. A. Blair, *Journ. Ind. Eng. Chem.*, **1**. 689, 1909; F. M. Stanton and A. C. Fieldner, *Tech. Paper U.S. Bur. Mines*, **8**. 7, 1912; I. C. Allen and I. W. Robertson, *ib.*, **26**. 3, 1912.

[3] W. C. Ebaugh and C. B. Sprague (*Journ. Amer. Chem. Soc.*, **29**. 1475, 1907; *Chem. News*, **96**. 240, 1907) use zinc oxide in place of magnesia. W. F. K. Stock (*Chem. News*, **30**. 211, 1874), and F. C. Garrett and E. L. Lomax (*Journ. Soc. Chem. Ind.*, **24**. 1212, 1905), prefer calcium oxide to magnesia, because it is more easily obtained free from sulphur.

[4] F. Hundeshagen (*Chem. Ztg.*, **16**. 1070, 1892; *Chem. News*, **66**. 169, 1892) says that sodium carbonate is not so efficient as potassium carbonate in retaining sulphur. J. O. Handy (*Journ. Anal. App. Chem.*, **6**. 611, 1892) considers that Hundeshagen's statement is of no significance in practice; and this agrees with the general opinion of those who use the process.

One gram[1] of the powdered[2] sample is intimately mixed in a 30-c.c. platinum[3] crucible with 3 grms. of Eschka's mixture,[4] and about 2 grms. more of this mixture is spread as a layer over the contents of the crucible to form a kind of cover. The open crucible is placed slant-wise on a triangle and heated with a sulphur-free flame—page 617. The mixture must be heated very gradually to drive off the volatile matter without risk of losing sulphur. A small escape of sulphur dioxide can be detected by its odour. The heating should never be such as to blacken the covering layer of Eschka's mixture. In about half an hour the lower half of the crucible is red-hot, and the temperature is raised until the crucible is red-hot. It is an advantage to stir the mixture occasionally with a platinum wire. When all the black particles have been burnt—a condition recognised by the grey colour of the mixture in the crucible changing to a yellow or yellowish-brown colour — the crucible and contents are allowed to cool.

Transfer the more or less pulverulent mixture to a 200-c.c. beaker, and digest it for about 30 minutes with 75 c.c. of hot water. Filter the clear liquid into a 300-c.c. beaker, and wash the residue twice by decantation; then transfer it to the filter paper, and wash it with water until the beaker contains about 200 c.c. of liquid. Add a slight excess of bromine water, about 4 c.c., and enough hydrochloric acid to make the solution slightly acid. Boil, and precipitate the sulphates with barium chloride as described on page 618.[5]

II. *Dry Fusion with Alkalies and Oxidising Agents.*

In these processes the sample is fused with sodium carbonate and potassium nitrate, or sodium nitrite (page 617), or ammonium nitrate,[6] and the residue taken up with water and evaporated with hydrochloric acid to expel the nitric acid before treatment with barium chloride. Fusion with sodium peroxide[7] offers many advantages; the chief disadvantage is the violence of the reaction with coal. To overcome this difficulty, Parr ignites the mixture in a closed bomb of about 30 c.c. capacity, as described below:

Parr's Process for Coal and Coke.—Intimately mix 0·7 grm. of finely powdered coke with 11·5 to 13 grms. of powdered and dry sodium peroxide[1] by means of a spatula in a 30-c.c. nickle crucible, cover the crucible, and insert a 3-inch fuse[2] under the cover, and extending well into the mixture. Support the crucible on a triangle in a dish with a layer of water $\frac{3}{4}$ inch deep. Ignite the fuse. In three or four minutes, when the mass has cooled, place the crucible and its cover in a small beaker. Add 30 c.c. of water. The mass dissolves in about two minutes. Rinse the crucible and cover; acidify the solution with hydrochloric acid; boil; add barium chloride in the usual way.

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[1] If 0·687 grm. of the sample be employed, every 0·001 grm. of barium sulphate represents 0·02 per cent. of sulphur.

[2] Large grains do not burn readily. If the powder passes a 60's lawn, it is generally satisfactory.

[3] A porcelain crucible can be used in place of a platinum crucible, but the combustion is then rather slower—particularly with coke.

[4] Eschka's Mixture.—Two parts of light calcined magnesia are intimately mixed with one part of anhydrous sodium carbonate. Three grms. of Eschka's mixture are mixed with one gram of the sample, and the whole is covered with a 2-grm. layer of the mixture. Calcined magnesia of commerce often contains sulphates. If the amount is considerable, it can be removed by boiling with sodium carbonate. A correction can be made for the sulphur in the sodium carbonate and magnesia by means of a blank experiment.

[5] H. Fresenius (*Zeit. anal. Chem.*, **13**. 346, 1874) remarks that the process gives the total sulphur. If calcium sulphate be present in the form of gypsum, the latter can be removed by boiling with sodium carbonate, etc. F. C. Calvert, *Chem. News*, **24**. 76, 1871.

[6] S. F. and H. E. Peckham, *Journ. Soc. Chem. Ind.*, **16**. 996, 1897; *Journ. Amer. Chem. Soc.*, **21**. 772, 1899; W. Koch and F. W. Upson, *ib.*, **31**. 1355, 1909; H. Schreiber, *ib.*, **32**. 977, 1910; A. C Langmuir, *ib.*, **22**. 99, 1900; J. Lidow, *Journ. Russ. Phys. Chem. Ges.*, **31**. 567, 1899; S. Aufrecht, *Pharm. Zeit.*, **41**. 469, 1896; R. Dubois, *Bull. Assoc. Chim. Belg.*, **15**. 225 1901; J. D. van Leeuwen, *Rec. Travs. Pays Bas*, **11**. 103, 1892.

[7] S. W. Parr, *Journ. Amer. Chem. Soc.*, **22**. 646, 1900; C. Sundstrom, *ib.*, **25**. 184, 1903; J. D. Pennock and D. A. Morton, *ib.*, **25**. 1265, 1903; T. W. Parr, W. F. Wheeler, and R Berolzheimer, *Journ. Ind. Eng. Chem.*, **1**. 689, 1909; F. V. Konek, *Zeit. angew. Chem.*, **22**. 516. 1903; T. St Warunis, *Chem. Ztg.*, **34**. 1285, 1910. H. Schillbach (*Zeit. angew. Chem.*, **16**. 1080, 1903) uses barium peroxide.

With coal, an intimate mixture of 0·7 grm. of finely powdered coal with 13 to 16 grms. of peroxide is compressed by means of a press or vice in a steel bomb.[3] A piece of No. 36 iron wire, 4 inches long, is inserted, one end under the mica gasket of the bomb, and touching the bomb; the other end is above the gasket and touching the cover. A current of 4 amps. applied to cover and bomb will fuse the iron wire and start the reaction. In two minutes cool the bomb in a little water. Unscrew the cover and proceed as indicated for coke. The test results by comparison with Eschka's process are quite satisfactory.

III. *Oxidation by Heating the Substance in a Current of Air or Oxygen, under Ordinary or under Reduced Pressure.*

Combustion Process for Pyrites in Clays, etc.—The determination of sulphur combined as pyrites can be effected in several different ways. The "combustion process" is as follows:—A hard glass tube, *A* (fig. 194)—length 40 cm.—is drawn out, and bent at right angles as shown at *B* in the diagram. One end of the glass tube is connected with a wash-bottle, *C*,[4] containing dilute potash solution (approximately 3N-KOH), and the other fitted with a pair of Volhard's absorption tubes,[5] *D* and *E*, each containing about 50 c.c. of an aqueous solution of potash.[6] 10–20 grms. of the finely powdered and dried

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[1] If too little peroxide is used, the reaction is explosively violent; if too much, the combustion is incomplete. Imperfect mixing leads to explosive or incomplete combustion. The peroxide must be rapidly weighed and brushed from the watch-glass with a glass brush.

[2] The fuse is made by nitrating cotton wick with a mixture of one part of fuming nitric acid (sp. gr. 1·5) and two parts of concentrated sulphuric acid (sp. gr. 1·84) for 12 hours at 15°. Wash for 12 hours in running water to remove all the acid. Dry at ordinary temperatures. When dry, digest it in a cold, nearly saturated solution of nitre for an hour. Press out the excess of solution and dry. Cut into 3-inch lengths for use.

[3] The bomb, fig. 193, is a cylinder of steel, $1\frac{1}{4}$ in. internal diameter; $1\frac{1}{2}$ in. internal depth; sides and bottom $\frac{1}{8}$ in. thick; flange $\frac{1}{8}$ in. around top; cover plate $\frac{3}{16}$ in. thick and $1\frac{3}{4}$ in. diam. The cover is clamped by a small clamp fitting under the flange of the bomb and pressing down the cover by a central screw. The cover is insulated from the bomb by a mica gasket, and from the screw of the clamp by ordinary red fibre.

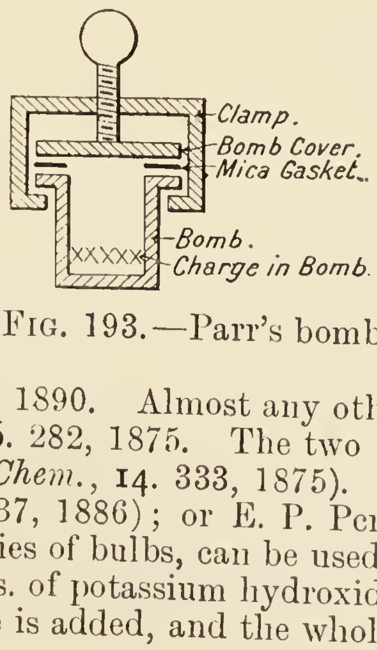

FIG. 193.—Parr's bomb.

[4] S. Schiff, *Chem. Ztg.*, 14. 233, 1890. Almost any other form will do quite well.

[5] J. Volhard, *Liebig's Ann.*, 176. 282, 1875. The two shown in the diagram are modifications by H. Fresenius (*Zeit. anal. Chem.*, 14. 333, 1875). M. Troilius' (M. Troilius, *Notes on the Chemistry of Iron*, New York, 37, 1886); or E. P. Perman's (*Chem. News*, 93. 213, 1906), or any of the numerous other varieties of bulbs, can be used in place of Volhard's.

[6] POTASH SOLUTION: 16·8 grms. of potassium hydroxide freed from sulphates by alcohol are dissolved in water, 1 c.c. of bromine is added, and the whole made up to 100 c.c.

(110°) clay is spread in a thin layer on the bottom of a long porcelain boat, which, in turn, is placed in the combustion tube at A. The end E is connected with an aspirator, and a current of air is drawn through the apparatus. The bubbles of gas should not pass through C more rapidly than admits of their being easily counted. The combustion tube is gradually heated to redness[1] in the vicinity of the boat containing the powder. Any deposit which forms in the tube in the vicinity of B should be driven forward by heating the tube with a Bunsen's burner, working the flame gradually from A to B. Any sulphur dioxide formed is oxidised by the bromine to sulphuric acid.[2] At the end of the combustion—about 30 minutes—the absorption vessel is removed and the contents are washed into a beaker. Any sulphates remaining in the tube AB are removed by drawing water up and down the narrow end by suction at F. The solution and washings are combined, and hydrochloric acid added to neutralise the free potash and to decompose the potassium hypobromite. The whole is boiled, and, if necessary, concentrated by evaporation. A hot aqueous solution of barium chloride is added, and the barium sulphate determined in the usual manner (page 618).

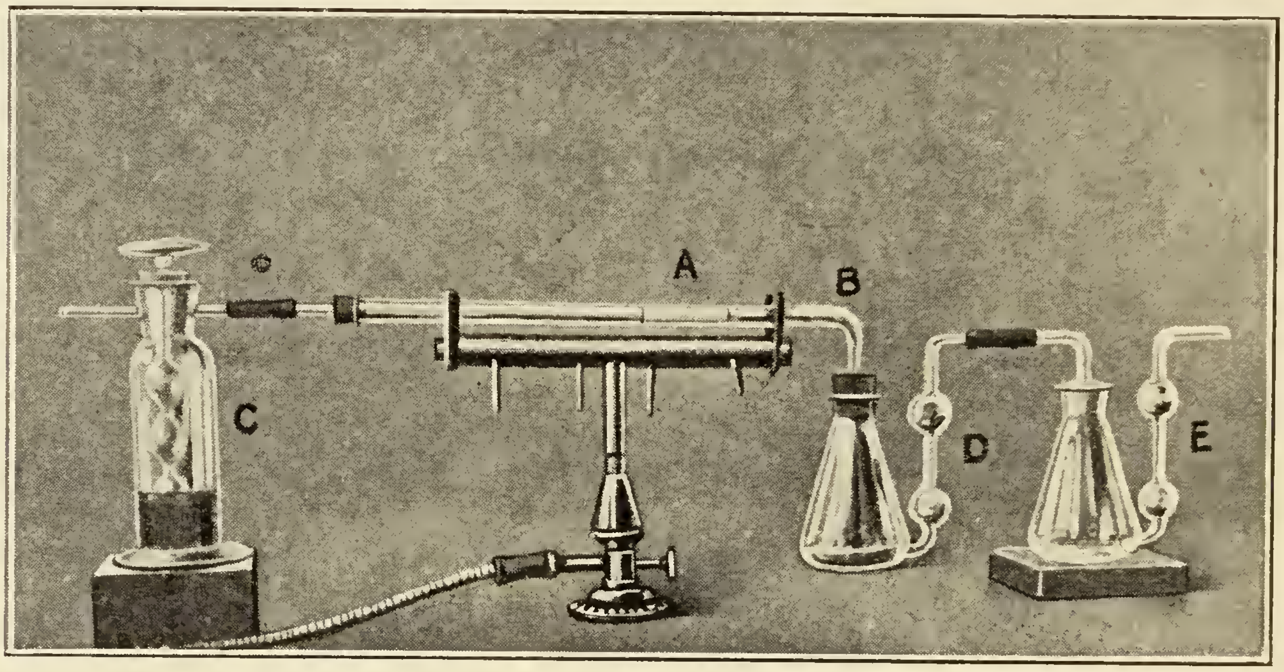

FIG. 194.—Determination of sulphides.

The clay is supposed to be free from calcium and magnesium carbonates; otherwise, calcium or magnesium sulphates may be formed, and the results will be correspondingly low. Water-soluble calcium and magnesium sulphates, however, might be determined before and after the combustion, and an allowance made for this disturbing reaction.

In some cases, say "*volatile sulphur*" *in fuels*, the combustion tube is packed towards the middle with about 5 cm. of platinised quartz or asbestos, instead of with copper oxide as in the combustion tubes, page 569. The substance under investigation is placed in a boat on one side of the platinised asbestos, and potash bulbs are fitted at the other end in the usual manner. The tube is heated very gradually, and a current of oxygen is passed through the system. The platinised asbestos ensures the oxidation of the sulphur dioxide, and the potash solution absorbs the sulphuric acid fumes.[1]

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[1] A Ramsay's attachment for an ordinary Bunsen's burner is convenient for this purpose. W. Ramsay, *Chem. News*, **49**. 2, 1883.

[2] Hydrogen peroxide is sometimes used in placed of bromine, and the sulphuric acid may be determined by titrating the standard potash solution used in D, E before and after the combustion. The clay is then supposed to be free from ammoniacal compounds, and the hydrogen peroxide from sulphur compounds. M. Fleischer, *Protocoll Sitz. Zentral-Moorkomm.*, **20**. 50, 1886; M. Berthelot and G. André, *Ann. Chim. Phys.* (6), **25**. 302, 1892; M. van Bemmelen, *Lands. Ver. Stat.*, **37**. 284, 1890; P. Jannasch, *Chem. Ztg.*, **14**. 566, 1890; *Zeit. anorg. Chem.*, **6**. 303, 1894; *Journ. prakt. Chem.* (2), **40**. 233, 1890; (2) **41**. 566, 1890; P. Jannasch, V. Wasowicz, K. Ashoff, and T. Bicks, *ib.* (2), **45**. 94, 1892; K. Zulkowsky, *Dingler's Journ.*, **241**. 52, 1881; L. P. Marchlewski, *Zeit. angew. Chem.*, **3**. 567, 1890; A. Sauer, *Zeit. anal. Chem.*, **12**. 32, 178, 1873; F. Muck, *ib.*, **14**. 16, 1875; W. Remmler, *ib.*, **33**. 75, 1894; O. Lindt, *ib.*, **4**. 370, 1865; W. G. Mixter, *Amer. J. Science* (3), **4**. 90, 1871.

Combustion in the Bomb Calorimeter.[2]—The combustion of 0·7 to 1·0 grm. of the sample in a bomb containing 10 c.c. of water with oxygen under a pressure of 30 to 40 atmospheres[3] is said to give results "more accurate and rapidly than all other methods." The apparatus is rather expensive, and hence is only used where a comparatively large number of determinations are made. There are several bomb calorimeters on the market, and specific directions for manipulating the bomb are supplied with the instrument. The treatment of the residue in the bomb is similar to that indicated above when dealing with Parr's process.[4]

IV. *Wet Treatment with Oxidising Agents under Ordinary or under High Pressures.*

The sample may be treated with various oxidising agents—potassium dichromate and fuming hydrochloric acid;[5] hydrogen peroxide,[6] nitric acid and potassium nitrate,[7] nitric acid under pressure,[8] etc. These methods are usually less convenient than the dry fusion processes.

Lunge's Wet Process[9] *for Pyrites.*—Warm 0·5 grm. of the given pyrites with about 100 c.c. of a mixture of 3 vols. of nitric acid (sp. gr. 1·4) and 1 vol. of concentrated hydrochloric acid, with occasional stirring, taking care to avoid loss by spurting. If free sulphur should separate, add cautiously a little potassium chlorate in order to oxidise the sulphur to sulphuric acid. Evaporate the solution to dryness on a water bath, and repeat the evaporation with 5 c.c. of concentrated hydrochloric acid until nitrous fumes cease to be evolved. Add 1 c.c. concentrated hydrochloric acid to the residue, and, in a few minutes, 100 c.c. of hot water. Filter and wash with hot water.[10] Treat the combined filtrate and washings with a moderate excess of ammonia; heat the solution to 60° or 70° for 10 to 15 minutes. The solution should then smell strongly of ammonia. Filter, and wash until the washings give no turbidity with barium chloride after standing for a few minutes. The combined filtrates should occupy about 250 or 300 c.c.[1] Acidify the solution with hydrochloric acid, avoiding an excess. Heat the solution to boiling; remove the flame; add, all at once,[2] barium chloride solution with constant stirring.[3] The addition of too great an excess of barium chloride leads to high results. Let the whole stand about 40 minutes. Decant the clear, filter, wash, etc., and weigh as barium sulphate.

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[1] C. F. Mabery, *Journ. Amer. Chem. Soc.*, **16.** 544, 1894; W. E. Barlow and B. Tollens, *ib.*, **26.** 341, 1904; W. G. Mixter, *Amer. Chem. Journ.*, **2.** 396, 1880; G. Brügelmann, *Zeit. anal. Chem.*, **15.** 1, 1876; **16.** 1, 1877; A. Sauer, *ib.*, **12.** 32, 1873; C. M. Warren, *Proc. Amer. Acad.*, **6.** 472, 1871; I. Bay, *Compt. Rend.*, **146.** 333, 1908; O. Dammer, *Zeit. angew. Chem.*, **22.** 440, 1909; O. Brunck, *ib.*, **18.** 1560, 1905; M. Holliger, *ib.*, **22.** 436, 1909; I. C. Allen and I. W. Robertson, *Tech. Paper U.S. Bur. Mines*, **26.** 8, 1912.

[2] I. C. Allen, W. A. Jacobs, and G. A. Burrell, *Bull. U.S. Bur. Mines*, **19.** 8, 1911; I. C. Allen, *Min. Scient. Press*, **81.** 569, 1900; R. Arnold, R Anderson, and I. C. Allen, *Bull. U.S. Geol. Sur.*, **398.** 265, 1910; I. C. Allen and I. W. Robertson, *Tech. Paper U.S. Bur. Mines*, **26.** 10, 1912; G. A. Filliti, *Bull. Soc. Chim.* (4), **21.** 338, 1899; N. W. Lord, *Prof. Paper U.S. Geol. Sur.*, **48.** 174, 1906; D. Lohmann, *Chem. Ztg.*, **35.** 1119, 1911.

[3] If a less pressure is used, there is a risk of incomplete combustion of the sulphur.

[4] If the bomb has a lead washer, the washings from the bomb are boiled for about 10 minutes with a 5 per cent solution of sodium carbonate, and then filtered, etc. This treatment decomposes any lead sulphate which may be formed.

[5] K. Charitschkoff, *Petroleum Zeit.*, **2.** 714, 1907.

[6] E. V. Lecocq and H. Vandervoort, *Bull. Soc. Chim. Belg.*, **16.** 181, 1902.

[7] F. W. Gill and H S. Grindley, *Journ. Amer. Chem. Soc.*, **31.** 52, 1909; A. Goetzl, *Zeit. angew. Chem.*, **14.** 1528, 1905; F. C. Calvert, *Chem. News*, **24.** 76, 1871.

[8] L. Carius, *Liebig's Ann.*, **136.** 129, 1865; *Zeit. anal. Chem.*, **4.** 451, 1865; G. Anelli, *Rass. Min. Met. Chim.*, **34.** 1, 1911; R. Holand, *Chem. Ztg.*, **7.** 99, 130, 1893.

[9] G. Lunge, *Zeit. anal. Chem.*, **20.** 417, 1881; *Zeit. angew. Chem.*, **2.** 473, 1889; *Fifth Int. Congress App. Chem.*, 399, 1906; E. Hintz and H. Weber, *Zeit. anal. Chem.*, **45.** 31, 1906.

[10] The residue may be dried, ignited, and weighed as a mixture of silica, silicates, and sulphates of lead, barium, calcium, etc. With calcareous or magnesian clays, there is a danger of loss as indicated above.

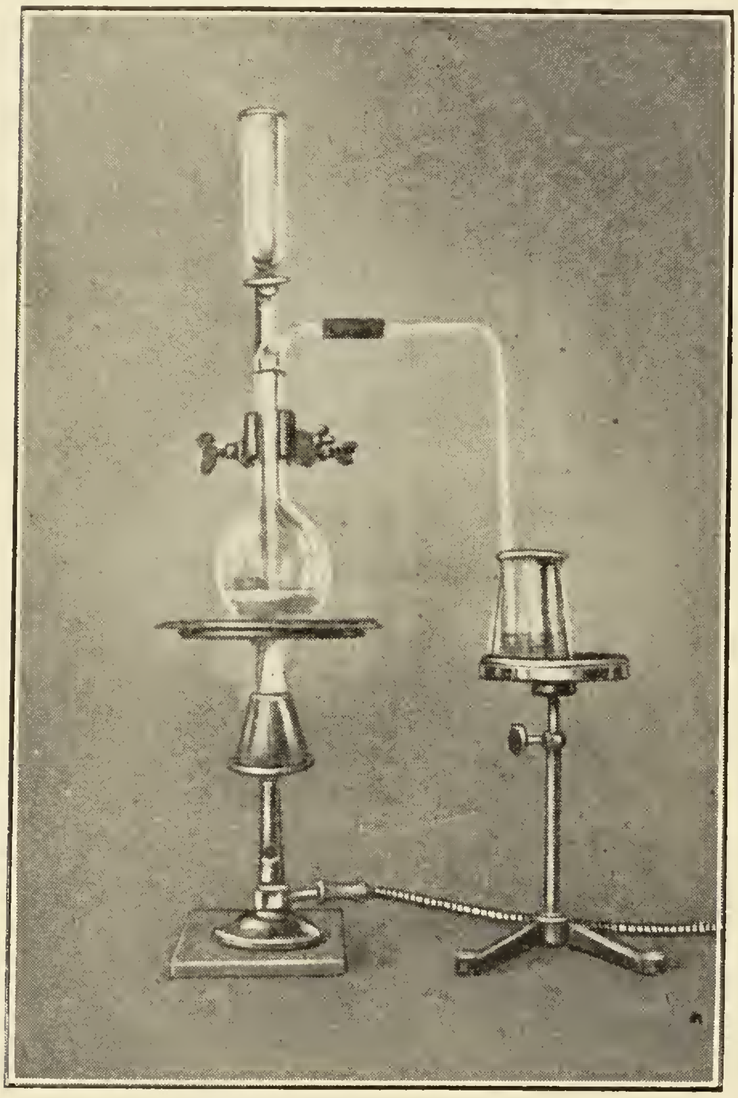

FIG. 195.—Determination of sulphides.

Sulphides decomposed by Acids.—When the sulphides—say sulphides of the alkalies or alkaline earths—can be decomposed by boiling acids,[4] grind, say, 5 grms. of the powder with water to a thin slurry. Transfer the slurry to a (250-c.c.) gas developing flask (fig. 195) fitted with a stoppered funnel, and an exit tube so that any gas generated may be passed through, say, 10 c.c. of a solution of cadmium acetate (or ammoniacal cadmium chloride).[5] Add hydrochloric acid to the mixture in the flask, *via* the stoppered funnel. Warm the contents of the flask, and drive off the hydrogen sulphide by a current of air which enters through the stoppered funnel. Add 10 c.c. of iodine solution to the cadmium acetate solution, and titrate the liberated iodine with standard sodium thiosulphate, as indicated on page 358.

There is a danger of losing sulphides when ferric salts are present. The hydrogen sulphide reduces the ferric salts and is itself oxidised. Hinrichsen[6] recommends adding, say, 10 c.c. of a 20 per cent. solution of stannous chloride to the mixture in the generating flask, in order to avoid the error.

Oxidisable Matter in Limestones.—The disintegration of limestones is supposed by some to be related with the amount of oxidisable matters, chiefly pyrites, which they contain,[7] and this is determined by the following process:—Add

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[1] If the volume is greater, concentrate by evaporation.

[2] See page 613.

[3] The adsorption error (page 611) is supposed to compensate the loss caused by the solubility of the barium sulphate in the mother liquid.

[4] F. A. Kuhnlenz, *Chem. Ztg.*, **31**. 835, 1907; F. L. Crobaugh, *Journ. Anal. App. Chem.* **7**. 280, 1893; T. J. Morrell, *Chem. News*, **28**. 229, 1873.

[5] CADMIUM ACETATE SOLUTION.—Dissolve 25 grms of cadmium acetate in 200 c.c. of glacial acetic acid, and make the solution up to a litre. F. Weil (*Compt. Rend.*, **102**. 1487, 1886) used a standard ammoniacal solution of a copper salt. After passing hydrogen sulphide through this solution, it was made up to a given volume, and an aliquot portion titrated as indicated on page 352 for unprecipitated copper. The difference between the result and the amount of copper originally present represented the amount precipitated by the hydrogen sulphide.

[6] F. W. Hinrichsen, *Mitt. k. Material-prüf. Amt.*, **25**. 321, 1895.

[7] A. M. Peters, *Journ. Amer. Chem. Soc.*, **25**. 143, 1903.

25 c.c. of $\frac{1}{10}$N-potassium permanganate to 1 grm. of the dried (110°) and powdered clay in a 250-c.c. Erlenmeyer's flask. When the powder is all moistened, add 100 c.c. of a 10 per cent. solution of sulphuric acid,[1] and shake the flask. If the colour of the potassium permanganate be discharged, add a second 25 c.c. of the permanganate solution. Heat the mixture on a water bath, with occasional shaking, for about half an hour.[2] Run 10 c.c. of $\frac{1}{10}$N-oxalic into the flask.[3] Let the mixture stay on the water bath a few minutes longer. All the brown manganic compounds should have passed into solution. The excess of oxalic acid is titrated with standard potassium permanganate. Three one-gram samples should be used. The results are calculated to "oxygen consumed by the limestone." A resistant limestone according to Peters' experiments, required less than 0·4 grm. of oxygen, while limestone which weathered easily required over 0·6 grm. of oxygen.[4] One gram of potassium permanganate, it will be remembered, furnishes 0·395 gram of oxygen (page 193).

§ 323. The Volumetric Determination of Sulphates—Raschig's Process.

Benzidine hydrochloride—$C_{12}H_8(NH_2)_2.2HCl$—in aqueous solution is hydrolysed in such a way that the solution behaves as if it contained neutral benzidine—$C_{12}H_8(NH_2)_2$—and hydrochloric acid. If such a solution be titrated with soda lye, the phenolphthalein will develop a pink coloration after all the acid is neutralised by the soda. The reaction is quantitative. Suppose, further, an excess of benzidine hydrochloride be added to a solution containing, say, sodium sulphate, sparingly soluble benzidine sulphate—$C_{12}H_8(NH_2)_2$—will be precipitated:

$$C_{12}H_8(NH_2)_2.2HCl + Na_2SO_4 = 2NaCl + C_{12}H_8(NH_2)_2.H_2SO_4.$$

The excess of benzidine hydrochloride can then be determined by titration with soda lye. The difference between the titre of the benzidine hydrochloride added to the sulphate solution, and that of the benzidine hydrochloride remaining after the precipitation of the benzidine sulphate, represents the "sulphate" in the given solution. This method, due to Müller, presupposes that the sulphate solution is exactly neutral. Since aluminium, iron, zinc, and other sulphates are not neutral, these bases should be absent. Some of the benzidine hydrochloride is also absorbed by the precipitated sulphate, and this leads to high results. The latter difficulty is less marked if the precipitation be effected in hot solutions.

Instead of proceeding by Müller's process, it is better to follow Raschig's variation,[5] and treat the precipitated benzidine sulphate with soda lye, using phenolphthalein as indicator. The end of the reaction is represented by the equation:

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[1] 110 c.c. of sulphuric acid (sp. gr. 1·84) and 1800 c.c. of water.

[2] Experiments show this to be sufficient to oxidise the pyrites, etc.

[3] More if necessary. The oxalic acid is adjusted so that at least 10 c.c. is present in excess of that which has been oxidised by the permanganate. If 25 c.c. of permanganate were added, 30 c.c. of oxalic acid will suffice, provided very little permanganate was reduced; otherwise more oxalic acid will be required.

[4] Phosphoric acid can be determined, if desired, in the solution by A. L. Emery's volumetric process (*Journ. Amer. Chem. Soc.*, **24**. 895, 1902); the insoluble residue is reported as "clay and sand."

[5] F. Raschig, *Zeit. angew. Chem.*, **16**. 617, 118, 1903; **18**. 331, 1905; **19**. 331, 1906; C. Friedheim and O. Nydegger, *ib.*, **20**. 9, 1907; W. Müller, *ib.*, **16**. 653, 1017, 1903; *Ber.*, **35**. 1587, 1902; W. Müller and K. Dürkes, *Zeit. anal. Chem.*, **42**. 477, 1903; G. von Knorre, *ib.*, **49**. 461, 1910; *Chem. Ind.*, **28**. 2, 1905; O. Nydegger, *Ueber die Bestimmung der Schwefelsäure durch Benzidin*, Bern, 1907; O. Huber, *Chem. Ztg.*, **29**. 1227, 1905; K. K. Järvinen, *Ann. Acad. Sci. Fennicæ*, **2**. iv, xvi, 1912; A. Heczko, *Zeit. anal. Chem.*, **50**. 748, 1912; **51**. 1, 1912; K. K. Järvinen, *Ann. Acad. Scient. Fennicæ*, **2**. A, 4, 1910; 16, 1911.

$$C_{12}H_8(NH_2)_2 . H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + C_{12}H_8(NH_2)_2.$$

The Precipitation.—Pour, say, 20 c.c. of the neutral or feebly acid solution of the given sulphate, with constant stirring, into 500 c.c. of a cold solution of benzidine hydrochloride[1] in a 600-c.c. Erlenmeyer's flask. Stir the mixture well with a glass rod. The voluminous crystalline precipitate of benzidine sulphate is allowed to settle for about 15 minutes, and then separated by suction through a Witt's filter plate (page 103)[2]—4 cm. diameter on the upper side, and 3·5 cm. on the lower side. The supernatant clear liquid is poured through the funnel, and the precipitate transferred by shaking the last fifth of the liquid before it is poured into the funnel. Any precipitate which sticks to the sides of the flasks in which the precipitation was made can be washed with some of the clear filtrate, or a special wash-bottle with benzidine solution can be used. Take care that no cracks appear in the precipitate as the last drop of mother liquid drains from the filter plate. Wash the precipitate twice with 5–10 c.c. of water[3] from a wash-bottle directed so as to wash down the sulphate adhering to the sides of the funnel. As the last of the wash-water drains off, disconnect the filtration flask from the pump.[4] This must be done before the precipitate contracts to a more or less dry silver-grey skin.[5]

The Transfer of the Precipitate to the Titration Flask.—The funnel is then inclined at an angle of about 45°, and a glass rod inserted through the stem of the funnel so as to turn the filter plate and precipitate over on to the walls of the funnel, with the plate uppermost. The filter plate is removed, and the precipitate transferred to a 250-c.c. Erlenmeyer's flask by the aid of a glass rod. The filter paper is squeezed into a roll, and also dropped into the flask. The funnel is placed against the mouth of the flask, and any adhering benzidine sulphate is washed into the flask with a vigorous jet of water. In all, about 25 c.c. of water should be used for the transfer. If any particles of the precipitate remain on the funnel, it is best to wipe them off with a small filter-paper swab, and transfer the latter to the flask. The benzidine sulphate should now be all in the flask. Close the flask with a rubber stopper and shake it thoroughly, so as to form a kind of slurry—precipitate, filter paper, and water—quite free from lumps of benzidine sulphate. Remove the stopper from the flask and wash back any adhering particles of the sulphate with a few drops of water.

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[1] BENZIDINE HYDROCHLORIDE.—Rub 40 grms. of benzidine thoroughly with 40 c.c. of water, and wash the "slip" into a litre flask with about 750 c.c. of water. Add 50 c.c. of concentrated hydrochloric acid (sp. gr. 1·9), and when all is dissolved to a clear brown solution, fill the flask up to the litre mark with water. If the solution be turbid, filter. For use, this solution is diluted with twenty times its volume of water. 150 c.c. will suffice for the precipitation of 0·1 grm. of H_2SO_4. Brown flecks may separate from the solution on long standing. These do no particular harm. Benzidine costs about 2s. 6d. per kilo.

[2] The filter plate is covered with two discs of moistened filter paper. The discs of filter paper are 4·6 cm in diameter. The projecting 3-mm. rim of the filter paper discs is carefully pressed against the sides of the funnel by means of a glass rod with a square end. Successful work depends upon the tight closing of the joint between the funnel and the filter paper.

[3] The benzidine sulphate is slightly soluble in water. By proceeding in this manner, the loss from this cause can be reduced to a minimum.

[4] Make sure that all the sulphuric acid has been precipitated, by testing the filtrate with barium chloride solution. No precipitate should be produced, but after standing 15 minutes a slight turbidity will probably appear owing to the decomposition of the trace of benzidine sulphate in the filtrate. The loss from this source is very small, and it is compensated by the slight excess of the $\frac{1}{10}$N-NaOH—one or two drops, corresponding with 0·12 to 0·2 per cent. of sulphur—required for colouring the phenolphthalein absorbed by the pulp of the filter paper in the flask during the titration.

[5] Dried benzidine sulphate cannot be properly distributed through the water, and, in consequence, it will be but slowly decomposed by the sodium hydroxide during the titration. The results will then be low. If by accident undecomposed flakes of benzidine sulphate should appear in the liquid, boiling with a small known excess of sodium hydroxide will effect decomposition. The excess of soda can be determined by back titration with standard acid.

The Titration.—Add about 2 c.c. of phenolphthalein,[1] and titrate the solution with $\frac{1}{10}$N-sodium hydroxide until the red colour of the indicator appears. Warm the flask over a flame until the colour has disappeared, and continue the titration until a faint red appears. Again heat the flask until the liquid boils, so as to expel the carbon dioxide. The end of the titration is represented by the appearance of a faint red colour in the liquid.[2] At the end of the titration one or two drops of $\frac{1}{10}$N-hydrochloric acid should remove the colour, and this should not reappear after boiling two minutes.

Example.—100 c.c. of a solution of sulphate were poured into 500 c.c. of the benzidine solution, and, after filtering, etc., the solution was washed with 20 c.c. of water. The benzidine sulphate slurry required 49·15 c.c. of $\frac{1}{10}$N-NaOH to develop the proper coloration. Here, 49·15 c.c. of $\frac{1}{10}$N-NaOH represent 0·2408 grm. of H_2SO_4. As a matter of fact, the solution really contained 0·2430 grm. of H_2SO_4. Hence, the error 0·0022 grm. approached 0·9 per cent. But closer results can be obtained after a little practice in the method.

Modification in the Presence of Iron Salts.—Nydegger tried the effect of slightly acidifying the solution with hydrochloric, nitric, and acetic acids; the effect of additions of potassium, ammonium, copper, aluminium, zinc, and chromium chlorides, potassium nitrate, sodium acetate, and ammonium, zinc, manganese, cobalt, copper, aluminium, and ferrous sulphates. The results were quite satisfactory. It is generally considered that no more iron should be present than is represented by Fe : S. If ferric iron be present, some will be occluded with the precipitated benzidine sulphate and spoil the result. The ferric iron should be reduced to the ferrous condition before adding the benzidine hydrochloride. The reduction is best made with hydroxylamine hydrochloride, as described below. Satisfactory results can then be obtained with both copper and iron pyrites.

For pyrites, Raschig recommends the following process:—0·8 grm. of finely powdered pyrites is placed in a dry 200-c.c. Erlenmeyer's flask with 5 c.c. of fuming nitric acid. Heat the mixture on a water bath, with a funnel in the neck of the flask to prevent loss by spurting. The pyrites should be decomposed in about half an hour. Add 30 c.c. of water, and warm the mixture a short time to dissolve the iron salts. Dilute the solution—with or without the removal of the solid residue—to the 100-c.c. mark in a measuring flask. Pipette 20 c.c. of this solution into a 600-c.c. beaker, and add 10 c.c. of a one per cent. solution of hydroxylamine hydrochloride, and 500 c.c. of the benzidine solution. Stir the mixture with a glass rod, and let it stand 15 minutes. Then proceed as described above.[3]

Errors.—With a little practice, the results obtained by this method for sulphur in pyrites, etc., rival in accuracy results with the barium chloride process. The more important sources of error are: (1) the slight solubility of the benzidine sulphate in water; (2) slight adsorption of benzidine hydrochloride by the precipitated benzidine sulphate; (3) imperfect titration due to the "balling" of the sulphate when it is overdried; (4) imperfect precipitation of sulphate through using insufficient benzidine hydrochloride; and (5) the need for a slight excess of the $\frac{1}{10}$N-NaOH solution, owing to adsorption of the indicator by the paper pulp. Some of these errors compensate one another. The time needed for the determination of sulphur in pyrites by this method is something less than one and a half hours, but the method is time-saving only when a number of determinations under similar conditions have to be made.

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[1] This unusually large amount of indicator is needed because some of the indicator is absorbed by the paper pulp in the flask.

[2] The tint can be recognised through the fibres of the filter paper, but, if necessary, the paper can be allowed to settle to facilitate the observation of the end coloration. An intense red colour shows over-titration.

[3] The number of c.c. of $\frac{1}{10}$N-NaOH used represents the per cent. of sulphur in the pyrites. The other four-fifths of the solution in the measuring flask can be used for check determinations.

§ 324. The Determination of the Soluble Salts in Clays.

The "soluble salts" in clays are responsible for certain manufacturing difficulties, and consequently it may be of great importance to determine their nature and amount. It is not sufficient to boil the clay with water and remove the soluble matters by filtration through filter paper, or by settling.[1] The clay is sometimes so finely divided that the solid cannot be separated from the liquid by filtration even through a dozen filter papers, and some clays take so long to settle that the solid matter appears to be in permanent suspension. The turbid filtrate may be evaporated to dryness on a water bath, and dried at 110°. The residue may then be extracted with water, and the filtrate will usually be quite clear.[2]

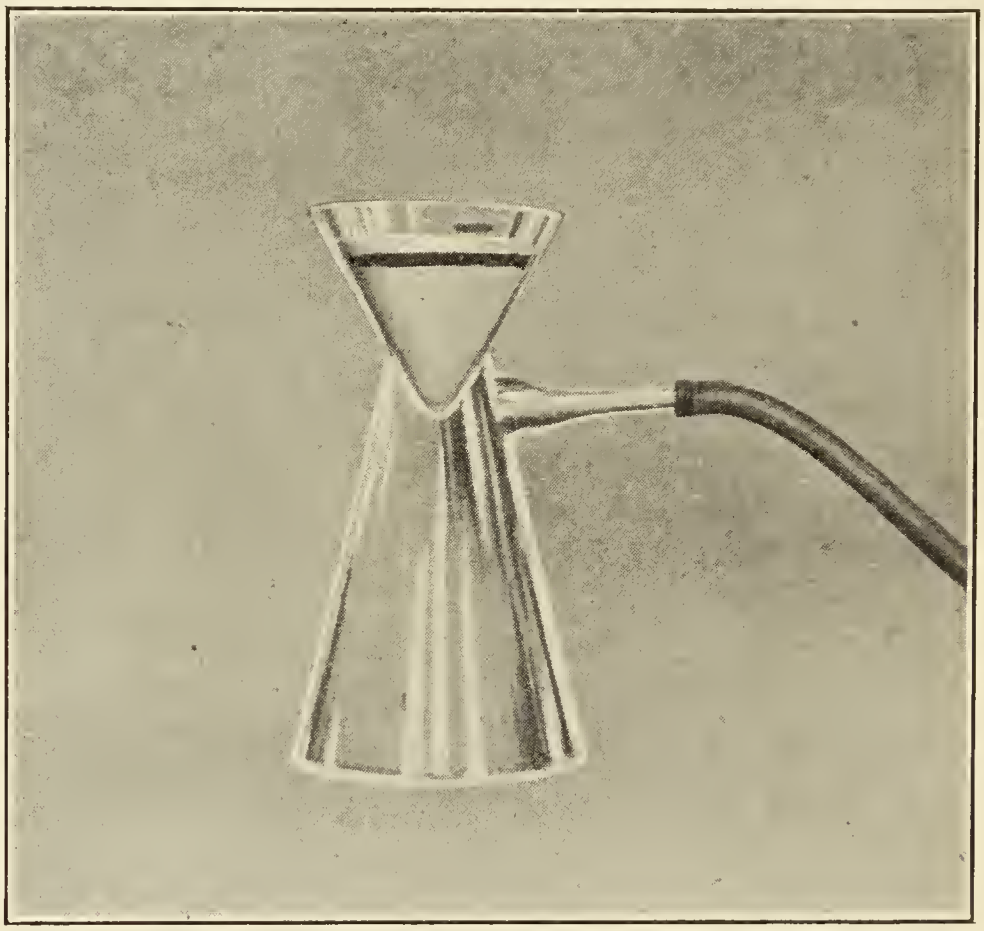

FIG. 196.—Filtration through porous cone.

The most satisfactory method is to filter the solution through biscuit pottery or alundum ware (page 621),[3] paper pulp, or similar filtration media.[4]

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[1] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2.** 666, 1887 ; London, **2.** 521, 1900.

[2] J. Post, *Chemisch-technische Analyse*, Braunschweig, **2.** 98, 1906.

[3] L. J. Briggs (*Bull. U.S. Agric. Dept.*, **19.** 31, 1902) and O. Schreiner and G. H. Failyer (*ib.*, **31.** 12, 1906) forced the solution through a Pasteur-Chamberlain water filter by means of a force-pump. J. W. Mellor, *Trans. Eng. Cer. Soc.*, **5.** 54, 1906 ; *Pot. Gaz.*, **32.** 1049, 1907 : C. E. Munroe, *Amer. J. Science* (3), **1.** 336, 1871 ; *Chem. News*, **24.** 79, 1871 : F. Klein, *Amer. J Pharm.*, **83.** 342, 1911 ; E. B. Forbes, *Journ. Ind. Eng. Chem.*, **4.** 544, 1912 ; G. L. Spencer, *ib.*, **4.** 614, 1912 ; M. A. Williamson and P. A. Boeck, *ib.*, **4.** 672, 1912 ; H. O. Anderson, *ib.*, **3.** 42, 1911 ; L. E. Saunders, *Met. Chem. Eng.*, **9.** 257, 1911 ; W. Pukall, *Ber.*, **26.** 1159, 1893 ; *Chem. News*, **72.** 86, 1895.

[4] E. Greiner, *Sprech.*, **42.** 399, 1909.

A Gooch's crucible in which the bottom of the crucible has neither been perforated nor glazed, or a biscuit crucible, can be glazed inside and outside to within half a centimetre from the bottom. This crucible is fitted up like the regular Gooch's crucible, fig. 56. Instead of using crucibles with a biscuit bottom, cones of porous earthenware can be used. These can either be fitted inside a suitable funnel, or fitted to the funnel-like neck of a Walther's filtration flask,[1] as indicated in fig. 196. The porous cone is fitted into the funnel by means of a rubber band, so as to make a tight joint. There is then no need for the perforated stopper.[2] Fig. 196 makes the arrangement clear. Rümpler's filtration cups,[3] made of thick, porous filter paper, are sometimes convenient for filtering solutions which give trouble with ordinary filter paper. Care should be taken to get the crucible[4] and filter paper to fit as indicated in the diagram, fig. 197. The inner layer in the diagram represents a section of the Rümpler's cup, and the outer layer, the crucible.

To conduct an experiment: boil about 5 grms. of the finely powdered clay with about 250 c.c. of water (distilled) in a resistance glass flask for about half an hour. Restore the water lost by evaporation from time to time. After the clay has settled somewhat, pour the liquid through the biscuit earthenware cone, fig. 196. The pump is now turned on, and the cone is kept filled with liquid. The residue is washed with hot distilled water, and the filtrate is evaporated to dryness in a weighed dish. The residue is dried at, say, 110°, and the amount of the residue is expressed as a percentage fraction of the original clay. The clay sometimes clogs the pores of the cone, so that filtration is extremely slow. In that case, the liquid can be filtered first through a Rümpler's cup (fig. 197), and afterwards through the biscuit cone. The washing should be conducted until a few drops of the liquid running from the clay leave no perceptible residue when evaporated to dryness on platinum foil. The result of this experiment does not necessarily represent the whole of the soluble salts in the clay. Some may be adsorbed by the clay in such a way that they can only be removed, if at all, by an extremely prolonged washing. However, the adsorbed salts which are not removed by washing are not of importance from the point of view of "soluble salts," and the result actually obtained is the datum required. The silica, alumina, etc., can be determined in the residue in the ordinary manner (pages 167 *seq.*).

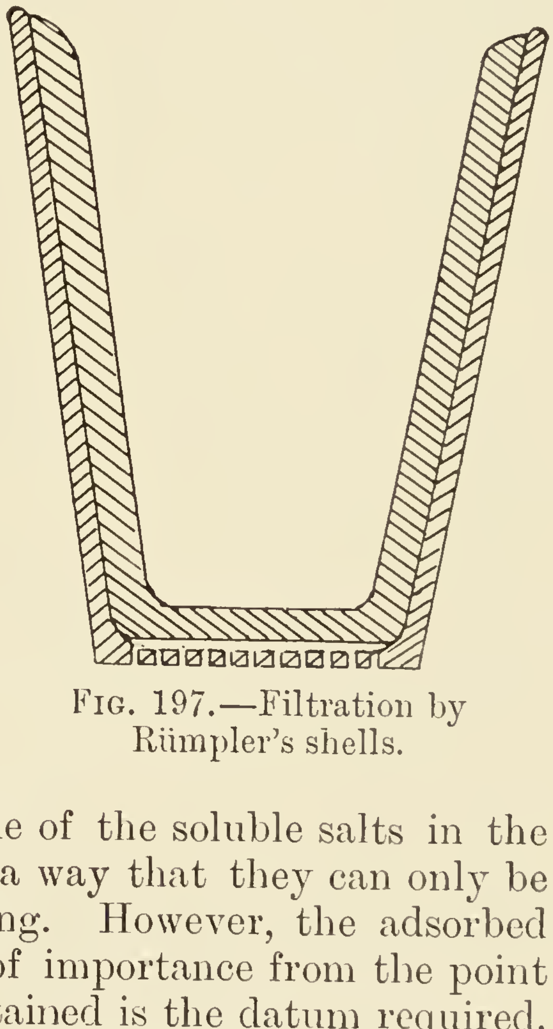

Fig. 197.—Filtration by Rümpler's shells.

§ 325. The Determination of Sulphates by the Turbidity Process.

The sulphates in the clear solution, say, from the preceding operation, can be determined as barium sulphate by the method of page 617; or, more rapidly, if a number of determinations have to be made, by comparing the turbidity of a solution containing a known amount of barium sulphate in suspension with that produced in the given solution by the addition of barium chloride. The solutions must be dilute enough to produce an opalescent, and not a settling precipitate. The opalescence depends largely on the size of the particles precipitated in the solution, and this, in turn, is determined by the physical condition of the solution—temperature, nature of other salts in solution, etc. The method gives fairly satisfactory results for industrial work when speed is a vital factor. The standard and the solution under investigation should not be widely different in strength, and, in consequence, a preliminary comparison should be made in test tubes. If the solution under investigation gives a very much more turbid solution than the standard, it should be diluted; and conversely. The solutions are not to be diluted *after* the addition of barium chloride.[1]

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[1] J. Walther, *Pharm. Centr.*, 530, 1898.

[2] The air in the rubber rings, under low pressure inside the flask—powerful suction—is apt to expand and burst the ring. Solid rubber rings do not work so well unless they are made of soft, very yielding rubber. These are not at present easily obtained.

[3] A. Rümpler, *Deut. Zuckerind.*, 29. 21, 1904.

[4] The cups fit crucibles 6·5 cm. high, 5·4 cm. upper diameter, and 3·2 cm. diameter at the base (outside measurements).

Standard Solution.—A standard solution of calcium sulphate is made by dissolving 0·9 grm. of calcium sulphate—$CaSO_4.2H_2O$—in a litre flask, so that 1 c.c. contains the equivalent of 0·0005 grm. SO_4. Make 25 c.c. of this standard solution up to a litre. Pipette, say, 100 c.c. into a wide-mouthed bottle. Add 0·1 to 0·2 grm. of powdered crystalline barium chloride and shake vigorously at intervals of 30 minutes. Pipette 50 c.c. of this solution into a Nessler's glass surrounded by black paper or a black velvet jacket.

Test Solution.—Make the solution from, say, 10 grms. of clay up to 250 c.c. with water; acidify with hydrochloric acid. Pipette, say, 100 c.c. of this solution into a tightly stoppered wide-mouthed bottle, and treat this as just described for the standard solution.

Comparison.—Place the test solution in a burette and run it into a Nessler's glass fitted with a black jacket, as indicated above, until the solutions in the two Nessler's glasses appear to have the same turbidity. The comparison is made with the Nessler's glasses resting upon a plate of clear glass supported over a sheet of black paper.

Calculations.—Suppose that the two solutions have the same turbidity when 13 c.c. have been run from the burette. Then 13 c.c. of the given solution have the same turbidity as 50 c.c. of the standard, *i.e.* as 0·000625 grm. SO_4. Hence, 250 c.c. will have the equivalent of

$$\frac{250 \times 0{\cdot}000625}{13} = 0{\cdot}012 \text{ grm. } SO_4.$$

Hence, 10 grms. of the clay have the equivalent of 0·012 grm. of SO_4; or, 0·12 per cent. SO_4; or 0·22 per cent. $CaSO_4$.

The most important disturbing influences arise from the introduction of side-lights during the comparison of the colours; and the mode of precipitation—hot or cold, with the solid salt or with an aqueous solution, and whether the readings be made at once or after the solution has stood some time. Consequently, *it is necessary to follow rigorously the same procedure in preparing the standard and the test solutions.*

Instead of employing Nessler's glasses for the comparison, Richards and Wells use a special instrument which they call a nephelometer, for comparing the turbidity of different solutions. Hind and Jackson read the depth of the turbid liquid at which a standard sperm or wax candle flame just ceases to be visible; the corresponding amount of SO_4 is read directly from a standard table prepared by empirical observations with solutions of known strength.[1] The cylinders are 3·5 cm. wide, 20 cm. high, and graduated from below upwards. The cylinder is supported over the lighted candle, and the liquid with the precipitate in suspension is poured in until the tip of the candle flame just disappears.

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[1] T. W. Richards and R. C. Wells, *Amer. Chem. Journ.*, 31. 235, 1904; *Journ. Amer. Chem. Soc.*, 27. 459, 1905; J. L. D. Hinds, *ib.*, 18. 661, 1896; 22. 269, 1900; *Chem. News*, 73. 285, 299, 1896; D. D. Jackson, *Journ. Amer. Chem. Soc.*, 23. 799, 1901; S. W. Parr and C. H. M'Clure, *ib.*, 26. 1139, 1904; S. W. Parr, W. F. Wheeler, and R. Berolzheimer, *Journ. Ind. Eng. Chem.*, 1. 689, 1909.

§ 326. The Amount of Barium Salt required to make the Soluble Sulphates in a Clay Innocuous.

Boil 40 grms. of the clay[2] in a long-necked flask with a litre of water. The soluble sulphates pass into solution. Add 1 c.c. of a standard solution of barium chloride containing 10 grms. $BaCl_2$ per litre. Shake the contents of the flask, and pipette about 2 c.c. of the contents on to a funnel fitted with a close-packed filter paper over a test tube. This test tube is labelled No. I. Add another cubic centimetre of the barium chloride solution, shake, and transfer about 2 c.c. to a second test tube, etc., labelled No. II. This operation is repeated with a series of test tubes ranged in order so that each tube represents 1 c.c. more barium chloride solution than the tube immediately preceding, and 1 c.c. less than the tube immediately succeeding. Add about 3 drops of dilute sulphuric acid to each test tube. That tube in which a turbidity first appears shows the tube which contains sufficient barium chloride to react with the sulphates. For instance, suppose that this is tube No. XIV., with 14 c.c. of barium chloride; and that the preceding one, No. XIII., with 13 c.c., is clear. The end of the titration is somewhere between these two tubes, say 13·5 c.c.[3]

Practice[4] shows that with the above proportions every cubic centimetre represents 1 lb. of barium carbonate to be mixed with a ton of clay to transform the soluble sulphates into insoluble and inert barium sulphate. Hence, in the example under consideration, 13½ lbs. of barium carbonate, or 6¼ lbs. of barium chloride,[5] are required per ton of clay. The results agree fairly well with practice, although the method has many faults. If much more than 20 c.c. of barium chloride be required, the soluble salt difficulty cannot be cured by the baryta method.

Seger and Cramer[6] have a more elaborate apparatus than that just indicated, but it requires less expert manipulation. The results are similar. Some clays —*e.g.* Wetley marl—give liquids very difficult to filter clear, and it is not then easy to determine the end of the barium chloride titration by the turbidity of the filtered solution. In that case, it is necessary to separate the solution from the clay by filtration through biscuit ware, as indicated page 630.

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[1] J. I. Hinds gives for SO_3 the relation $y = 0·0482 \div x$, where x is the cylinder reading, and y the percentage value of SO_3 sought; and for CaO when the lime is precipitated as calcium oxalate $y = 0·036 \div (x - 0·3)$. Different cylinders, and different amounts of raw material, would, of course, require different formulæ.

[2] Air-dried, or natural undried clay, or clay dried at 110°.

[3] C. Beringer and J. J. Beringer, *Chem. News*, **59**. 41, 1889; R. Wildenstein, *Zeit. anal. Chem.*, I. 432, 1862.

[4] B. Kerl, *Handbuch der Tonwaarenindustrie*, Braunschweig, 71, 523, 1906.

[5] Relatively more of the insoluble carbonate is needed because of the mixing difficulty. The soluble chloride is relatively easily brought in contact with the sulphates.

[6] H. A. Seger and E. Cramer, *Tonind. Ztg.*, **18**. 637, 1894; *Hilfs-Geräte für Beaufsichtigung und Vervollkommnung des Betriebes von Ziegeleien*, Berlin, 96, 1911.

CHAPTER XLIII.

THE DETERMINATION OF THE HALOGENS.

§ 327. The Detection of Fluorides.

THERE is no certain direct test for fluorides in silicates. The two most important reactions available for qualitative tests are (1) the evolution of hydrogen fluoride, which occurs when a fluoride is heated with concentrated sulphuric acid. The reaction is expressed in chemical symbols: $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$. The presence of the hydrogen fluoride is recognised by its action on glass—the so-called "etching test." (2) If silica or a silicate be present, most of the hydrogen fluoride reacts with the silica to form silicon fluoride—SiF_4—as indicated by the symbols: $SiO_2 + 4HF \rightarrow 2H_2O + SiF_4$. The silicon fluoride will not etch glass, but it will react with a drop of water, forming hydrofluosilicic and silicic acids. Thus, in symbols: $3SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3$. The latter gives the drop of water a turbid appearance—the so-called "hanging drop test." If the silicate contains fluorides which are not attacked by the concentrated acid, it is necessary to get the fluoride in a form—say, as calcium fluoride—susceptible to attack before either test can be applied.

The Separation of Fluorine as Calcium Fluoride from Fluo-Silicates not attacked by Sulphuric Acid.[1]—Mix the fluo-silicate with about eight times its weight of sodium carbonate, fuse the mixture in a platinum crucible, and when the mass is cold extract with water. The solution contains sodium fluoride and sodium silicate. Remove the silica by adding an excess of Schaffgotsch's solution, and allow the mixture to stand overnight in a warm place. Filter, and evaporate the filtrate to a small volume. Add a little phenolphthalein, and carefully add dilute hydrochloric acid from a burette until the red colour of the solution disappears. To make sure the mass is just neutralised, and no excess of acid is present, heat the solution to boiling—the red colour will reappear as the solution cools—and repeat the addition of hydrochloric acid, etc., until the solution is only faintly coloured on boiling. Add an excess of a solution of calcium chloride, and again boil the solution. Filter off the precipitate, wash, dry, and ignite in a platinum crucible. Add acetic acid, and evaporate to dryness. This converts any calcium carbonate into soluble acetate. Rub up the mixture with water, and filter off the insoluble calcium fluoride. Dry and burn off the filter paper. The powder is then ready for the etching test.

The Etching Test.—This is available for fluorides which are free from silica or silicates, and are attacked by concentrated sulphuric acid. A small clear glass plate, free from scratches, is thoroughly cleaned and warmed. A little molten wax[2] is poured on to the warm plate, and the excess drained off, so that a thin uniform layer of wax remains spread over the plate. The plate is allowed to cool in a horizontal position. While the wax is still warm, make a small ✠ on the wax with a pointed instrument, so as to lay bare, but not to scratch, the glass.[1]

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[1] F. P. Treadwell, *Analytical Chemistry*, New York, I. 352, 1903.

[2] Beeswax; or, better, melt together equal weights of carnauba wax and paraffin wax, and thoroughly mix by stirring.

The powder under investigation is placed in a platinum crucible,[2] along with 2 or 3 c.c. of concentrated sulphuric acid.[3] Warm the upper edge of the crucible cautiously and quickly with a small flame. Press the glass plate, waxed side downwards, upon the crucible so that the cross is in the centre and the crucible is sealed to the plate when the wax cools. The crucible is supported in a hole in a piece of thick asbestos board, cut so as to fit the crucible tightly. Put two or three drops of water on the glass plate and press the end of a condenser[4] (fig. 199) down on to the plate.[5] Heat the crucible for about half an hour over a small flame—9 mm. high, and 6 mm. below the bottom of the crucible. The disposition of the apparatus will be obvious from fig. 198, where *C* is the condenser, *B* the glass plate, *A* the asbestos board and crucible, and *D* the micro-burner for heating the crucible.[6] When the mixture has been heated for about an hour, remove the condenser and plate. Warm the plate a little, and wipe off the wax. Clean the plate on both sides with polishing powder which will not scratch the glass. Examine the plate by reflected light for any etching. A test should not be considered positive unless the cross can be seen from both sides of the glass.[7]

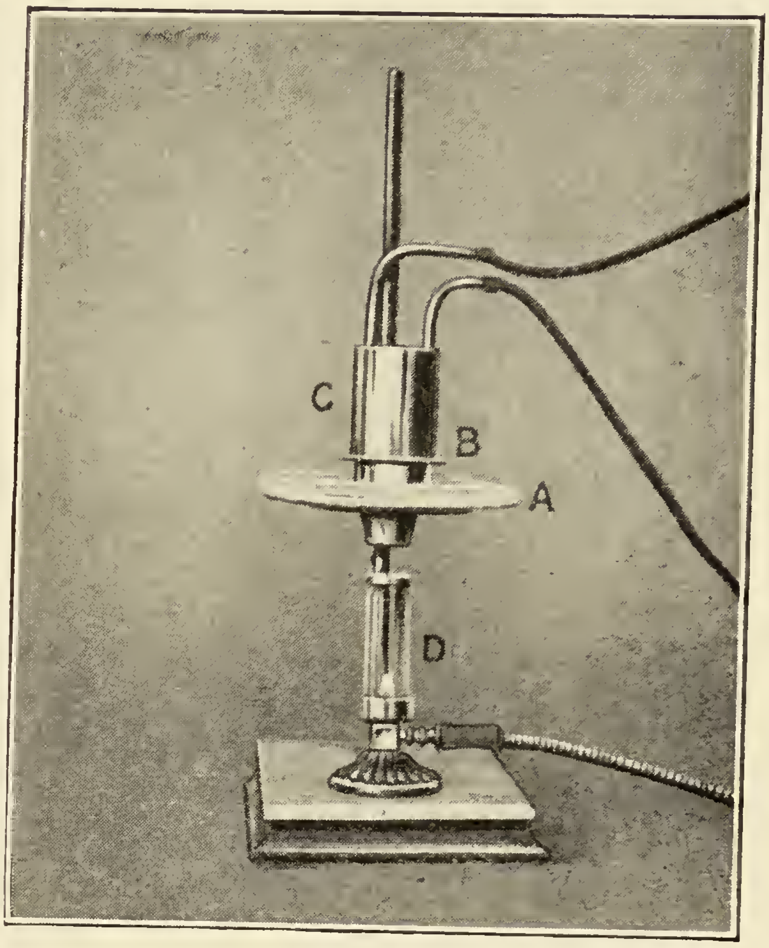

Fig. 198.—Etching test for fluorides.

Woodman and Talbot[8] state that their process, as described above, will give a recognisable test, that is, the cross will be visible from both sides of the plate, with 1 : 5,000,000 parts of fluorine. The temperature is an important factor. It is not possible to estimate the amount of fluorine from the intensity of the etching,[1] but Woodman and Talbot obtained promising results by varying the temperature of the crucible. Thus, they state:

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[1] The marks are best made about 1 mm. wide, and the two arms of the cross about 4 mm. long. The ends of the arms of the cross should be marked on the uncoated side of the glass with a scratching diamond or file.

[2] It is best to have everything in the crucible quite dry, since the etching is not always so well defined if moisture be present.

[3] The sulphuric acid must be free from fluorides. This can be determined by a blank experiment. If fluorides be present, they can be removed by diluting the acid with water and evaporating down to its former volume.

[4] According to Woodman and Talbot, a suitable condenser is made from a tube resembling a carbon filter tube by stretching a piece of sheet rubber (such as is used by dentists) over the wide end. The diameter of the tube should be wider than the platinum crucible; the narrow end is fitted with the necessary inlet and outlet tubes.

[5] The etching is frequently done on the convex side of a waxed watch-glass, and a little cold water is kept in the watch-glass to prevent the wax melting, covering the cross with wax, and so stultifying the test.

[6] It is advisable every now and again to put a couple of drops of water on the plate round the edge of the condenser to keep the wax from melting.

[7] Sulphuric acid may corrode the glass so that the cross can be seen when the glass is breathed upon. The scouring with the polishing powder usually removes the sulphuric acid "stain."

[8] A. G. Woodman and H. P. Talbot, *Journ. Amer. Chem. Soc.*, **28**. 1437, 1906; **29**. 1362, 1907; C. Blarez, *Chem. News*, **91**. 39, 1905; A. E. Leach, *Ann. Rep. Mass. State Board of Health*, **36**. 309, 1905; G. W. M. Williams, *Chem. World*, **1**. 255, 1912.

Table LXXIII.—Test Analyses for the Detection of Fluorine.

Temperature.	Distinguishes one part of fluorine per
79– 82°	25,000– 100,000
113°	100,000– 1,000,000
136°	1,000,000– 5,000,000
173–178°	5,000,000–25,000,000
213–218°	less than 25,000,000

This test is of very limited application so far as the silicate industries are concerned, because the complete absence of silica is essential if but small quantities of fluorine are in question.

The Hanging Drop Test.—About half a gram of the thoroughly dried powder under investigation is well mixed with about 0·1 grm. of dried precipitated silica and placed in the bottom of a test tube about 5 cm. long and 1 cm. wide. The test tube *A* (fig. 199) is fitted with a one-hole rubber stopper, *B*. The stopper carries a piece of glass tubing, *C*, closed at one end, and inserted in the stopper so that the open end of the tube extends about 3 mm. below the stopper. The glass tubing *C* is nearly filled with two drops of water, *D*, from a small pipette. The stopper and everything else inside the test tube must be quite dry. Pipette 1 or 2 c.c. of concentrated sulphuric acid into the test tube, and immediately insert the stopper without dislodging the drop of water in the little tube. Place the test tube in a beaker of water. Heat the water to boiling, and, after 20–30 minutes' heating, if the substance contains appreciable quantities of fluorine, a heavy gelatinous ring of silicic acid will be found at the mouth of the little tube carrying the drop of water.[2] With a little practice, or by conducting the test simultaneously with powders containing known amounts of fluoride, a rough idea can be formed how much fluorine is present, and whether the compound is worth a quantitative investigation by, say, Oettel and Hempel's process (page 646). Carbonates should not be present, or the stopper may be blown

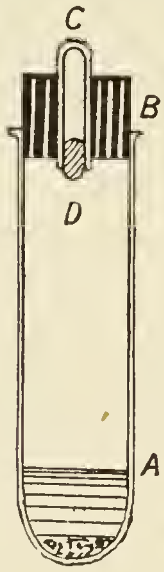

Fig. 199.—Hanging drop test for fluorides.

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[1] H. Ost, *Ber.*, **26**. 152, 1893; but see O. Renner, *Ueber die Bestimmung des Fluors*, Weida, i. Th., 1912.

[2] W. Kopp (*Ber. König. Sächs. Ges. Wiss.*, 37, 1882) has modified the test. A small flask with exit tube is thoroughly dried, and a mixture of the finely powdered material with the precipitated silica is placed in the flask. Pour an excess of concentrated sulphuric acid into the flask. One end of a delivery tube is fitted to the flask, and the other end dipped into a small cylinder containing a decigram of colourless aniline (or ammonia) in 30 c.c. of water. Heat the flask to 50° or 60°. A white deposit about the part of the delivery tube which dips into the aniline indicates the presence of fluorine. The white glistening crystalline solid—aniline silicofluoride—which forms in the liquid may be digested with a solution of caustic soda in absolute alcohol, and sodium silicofluoride will be formed. See also P. E. Browning, *Amer. J. Science* (4), **32**. 249, 1911; E. Rupp, *Zeit. Nahr. Genuss.*, **22**. 496, 1911; A. Sartori, *Chem. Ztg.*, **36**. 229, 1912; A. Kickton and W. Behncke, *Zeit. Nahr. Genuss.*, **20**. 193, 1910.

from the tube or the tube burst. Hence, carbonates should be destroyed by calcination before the test is applied.

§ 328. The Gravimetric Determination of Fluorine as Calcium Fluoride.

The fluorides in many silicates are not decomposed by digestion with sulphuric acid, and, in consequence, it is necessary to get such fluorides into solution before the analysis can be made. When much fluorine is present the silica must be determined by a special process, because part will be volatilised as silicon tetrafluoride when the aqueous extract of the sodium carbonate fusion is evaporated to dryness, etc.

According to Deville and Fouque,[1] the "loss on ignition" can be determined without losing fluorine, since the decomposition of the calcium fluoride requires a higher temperature than for the expulsion of water.[2] Alkaline fluorides, however, volatilise at a comparatively low temperature. Thus, 0·549 grm. of sodium fluoride lost 0·4 per cent. in weight when heated for about 6 minutes in the full flame of a Bunsen's burner; 0·2714 grm. of sodium fluoride lost 1·4 per cent. in weight under the same conditions; while no appreciable loss could be detected after heating 15 minutes with the flame just sufficient to redden the bottom of the platinum crucible.[3]

The methods for the isolation of the fluorides are rather tedious. That usually employed is based upon one proposed by Berzelius and Rose.[4] The compound is decomposed by fusion with alkaline carbonate—with or without silica. Silica and the bases are precipitated from the solution of the fused cake with ammonium carbonate, ammoniacal zinc oxide (Berzelius' solution), or ammoniacal mercuric oxide (Seemann's solution), and from the resulting solution, calcium or barium fluoride, together with the oxalate, sulphate or carbonate, are precipitated from the filtrate. The carbonate, etc., is removed by acetic acid, and calcium fluoride remains.[5]

The First Silica Precipitation.—Two grams of the uncalcined silicate are fused in a platinum crucible with about 12 grms. of sodium carbonate[6] without the blast.[7] The resulting cake is leached with water, filtered, and washed. Some of the silica, sodium zirconate, barium and calcium carbonates, if present, remain on the filter paper.[8] This and all the other precipitates are reserved for the determination of silica, etc.

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[1] H. St C. Deville and F. Fouque, *Compt. Rend.*, **38**. 317, 1854. See page 639.

[2] If there is any danger of loss of fluorine during ignition, G. Tammann (*Zeit. anal. Chem.*, **24**. 343, 1885) recommends adding a large excess of sodium carbonate or barium hydroxide.

[3] S. Waldbott, *Journ. Amer. Chem. Soc.*, **16**. 418, 1894.

[4] J. J. Berzelius, *Pogg. Ann.*, **1**. 169, 1824; H. Rose, *ib.*, **79**. 115, 1850; T. M. Chatard, *Trans. Amer. Inst. Min. Eng.*, **21**. 170, 1893; F. Wyatt, *The Phosphates of America*, New York, 149, 1892; T. Korovaeff, *Journ. prakt. Chem.* (1), **85**. 442, 1862; P. Jannasch, *Neues Jahr. Min.*, **2**. 123, 1883; A. A. Koch, *Journ. Amer. Chem. Soc.*, **29**. 1126, 1907; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 184, 1910; L. Fricke, *Stahl Eisen*, **24**. 889, 1904; E. Zdarek, *Zeit. physiol. Chem.*, **69**. 127, 1910; K. Daniel, *Zeit. anorg. Chem.*, **38**. 257, 1904.

[5] Small amounts of fluorine can also be determined colorimetrically with advantage—page 644.

[6] Calcium fluoride cannot be completely decomposed by fusion with sodium carbonate, but the decomposition is complete if the fluoride be mixed with silica or a silicate. Hence, if the fluorides be high, and the silica low, the addition of 3 grms. of silica is recommended to ensure complete decomposition (page 647). This is not usually needed for Cornish stone, nor for glazes.

[7] G. Forchhammer stated that all the fluorine is not obtained by melting silicates, *e.g.* topaz or tourmaline, with sodium carbonate; and Städeler states that if the lid be removed during the fusion there will be a loss of fluorine (*Journ. prakt. Chem.* (1), **99**. 66, 1866).

[8] If sulphur, zirconium, and chlorine are to be determined, the solution from the fused cake can be made up to 250 c.c. Take 50 c.c. for the sulphur; 100 c.c. for the fluorine; and 100 c.c. for the chlorine. But the solutions may be so dilute that it is advisable to use a separate sample for these determinations rather than take a correspondingly greater amount of the original sample for this fusion.

The Second Silica Precipitation.—The filtrate contains the fluorine as alkaline fluoride. Introduce 10 grms. of solid ammonium carbonate,[1] and digest the mixture for about 12 hours at about 40°, whereby silica and alumina are precipitated. Filter and wash the precipitate with aqueous ammonium carbonate. The filtrate still contains some silica.

The Third Silica Precipitation.—Evaporate the filtrate to dryness;[2] digest the mass with water; and neutralise the solution very carefully with nitric acid, as recommended by Treadwell,[3] with phenolphthalein as indicator: Add 2N-nitric acid from a burette until the pink colour of the indicator has disappeared. Heat the solution to boiling, and the red colour reappears. When cold, again discharge the colour of the indicator; heat to boiling as before, and repeat the operations until the addition of $1-1\frac{1}{2}$ c.c. of 2N-nitric acid suffices to discharge the colour. Add 5 c.c. of Seemann's solution,[4] and evaporate the mixture until the smell of ammonia has disappeared. Ammonia interferes with the subsequent precipitation of calcium fluoride. The precipitate contains traces of silica and mercury oxide.[5] Filter off the precipitate, and wash with water.

The Precipitation of the Fluoride as Calcium Fluoride.—Add nitric acid to the filtrate until the alkaline carbonate is nearly decomposed. If too much acid be present, a little more sodium carbonate must be added, so that the solution is distinctly alkaline. Boil with a large excess of an aqueous solution of calcium chloride.[6] Calcium carbonate and fluoride are precipitated.[7]

The Removal of Calcium Carbonate.—Collect the precipitate on a filter paper,[8] wash with hot water, dry, and ignite slowly to faint redness,[1] in a platinum crucible.[2] Add dilute acetic acid in excess[3] of that needed to dissolve the calcium oxide and carbonate. Heat in a covered crucible on a water bath until effervescence ceases. Evaporate to dryness. Digest the residue in water very slightly acidulated with acetic acid.[4] Filter, wash, and ignite the precipitate. If much fluorine be present, the digestion with acidulated (acetic) water may be repeated. The complete removal of calcium oxide and carbonate is shown by the absence of residue when a drop or two of the filtrate is evaporated to dryness on a piece of platinum foil. The last filter paper and contents with the precipitated calcium fluoride are ignited gently to faint redness in a platinum crucible—this temperature just suffices to burn off the filter paper—the crucible and contents are then weighed.

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[1] Not the nitrate or chloride, in order to avoid loss on evaporation.

[2] The liquid is inclined to froth and spit during the evaporation, owing to the decomposition of the ammonium carbonate. Hence, the dish must be covered by a clock-glass as long as there is any danger of loss. Wash the clock-glass, and of course let the washings run into the basin.

[3] F. P. Treadwell, *Kurzes Lehrbuch der analytische Chemie*, Leipzig, 2. 389, 1911.

[4] SEEMANN'S SOLUTION.—Moist, freshly precipitated mercuric oxide (about 20 grms.) is dissolved to saturation in Schaffgotsch's solution. The mercuric oxide is made by adding an aqueous solution of sodium hydroxide to a hot saturated solution of mercuric chloride, and the precipitate is washed with hot water until a portion of the precipitate volatilises on platinum foil without residue—F. Seemann, *Zeit. anal. Chem.*, 44. 343, 1905.

BERZELIUS' SOLUTION.—A solution of ammonio-zinc oxide, as originally recommended by J. J. Berzelius (*l.c.*), is sometimes employed for the purpose as Seemann's. Precipitate an aqueous solution of pure zinc sulphate with caustic potash. Filter, wash by decantation, and dissolve the precipitate in ammonia—M. Kleinstück, *ib.*, 50. 697, 1912.

[5] And phosphorus, if all was not precipitated with the alumina. Test with a solution of ammonium molybdate. If phosphorus be present, add an excess of silver nitrate solution. This precipitates silver phosphate and carbonate. Warm the solution in order to coagulate the precipitate, and filter. Precipitate the excess of silver nitrate with an aqueous solution of sodium chloride (2E). Boil the solution to coagulate the silver chloride, and filter. Add a little sodium carbonate until the solution reacts alkaline. The same procedure removes any chromate as silver chromate—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 422. 186, 1910.

[6] CALCIUM CHLORIDE SOLUTION.—Dissolve 21·93 grms. of the crystalline salt ($CaCl_2 . 6H_2O$) in 100 c.c. of water (2E).

[7] G. Starck and E. Thorin (*Zeit. anal. Chem.*, 51. 14, 1912) add a known amount of oxalic acid and precipitate the fluorine with calcium oxalate by the addition of calcium chloride in a solution slightly acidified with acetic acid. The precipitate is filtered on asbestos, dried at 210°, and weighed. The calculated amount of calcium oxalate is deduced, and the difference represents calcium fluoride. G. Starck (*Zeit. anorg. Chem.*, 70. 173, 1911; G. Starck and E. Thorin, *Zeit. anal. Chem.*, 51. 14, 1912) adds lead chloride to precipitate lead chlorofluoride—PbFCl. This precipitate has a high molecular weight (page 332). The method has not been thoroughly tested, but it promises well.

[8] Calcium fluoride alone gives a slimy precipitate which is very difficult to filter, but in the presence of calcium oxalate or carbonate it filters better. The calcium fluoride is sparingly soluble in hydrochloric and nitric acids, and almost insoluble in acetic acid. The precipitate is more soluble in the presence of ammonium salts.

Verification of the Result.—That the precipitate is really calcium fluoride should be confirmed by converting the calcium fluoride into calcium sulphate by the addition, drop by drop, of concentrated sulphuric acid. Drive off the excess of acid by evaporation, and test the fumes for hydrogen fluoride by means of a greased glass plate in the usual manner. Gradually raise the temperature to a red heat. Cool, and weigh. One gram of CaF_2 should give 1·7436 grms. $CaSO_4$. If the weights are not concordant, as they rarely are, the impurity may be silica, calcium silicate, or calcium phosphate arising from the imperfect separation of silica and phosphorus. Calcium sulphate may also be present, due to the imperfect washing of the precipitate. Phosphorus can be detected by the ammonium molybdate process in the hot nitric acid solution. It is difficult to decide whether the impurity be calcium silicate or silica. In the case of the phosphate and silicate, these constituents may be decomposed by the sulphuric acid treatment; but in the case of silica and calcium sulphate, it is possible to calculate the amount of calcium fluoride from the observed increase in weight. If the observed increase in weight be multiplied by 1·3448, we get the corresponding amount of calcium fluoride; and by 0·6543, the corresponding amount of fluorine. The *raison d'être* of the calculation will appear from the equation:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF,$$

where 136·16 represents the molecular weight of calcium sulphate, and 78·09, the molecular weight of calcium fluoride. Hence, when the sulphuric and hydrofluoric acids have been driven off, an increase in weight of 58·07 grms. will represent 78·09 grms of calcium fluoride, or 38 grms. of fluorine. Hence, if w represents the increase in weight obtained by the action of sulphuric acid on the given sample, the corresponding amount x of fluorine will be as $58{\cdot}07 : w = 38 : x$; or,

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[1] A slight loss of fluorine may occur by ignition of the filter paper in contact with calcium fluoride. G. Tammann, *Zeit. anal. Chem.*, **24**. 328, 1885; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 186, 1910. W. Hempel (*Gasanalytische Methoden*, Braunschweig, 347, 1900) found that 1·5 grms. heated 15 minutes at 1000° lost 0·019 grm.; and at a dull red heat, 0·005 grm. F. Seemann (*Zeit. anal. Chem.*, **44**. 343, 1905) noticed a loss of 0·0008 grm. when a gram was heated over a Teclu's burner at 1000°; and F. P. Treadwell and A. A. Koch (*Zeit. anal. Chem.*, **43**. 469, 1904) found a loss of 0·0002 grm. after ignition for 10 minutes over a Teclu's burner, and 0·0009 grm. after half an hour's heating.

[2] Instead of carrying this process any further, we may proceed to page 641.

[3] If the precipitate were treated directly with the acetic acid, without the preliminary ignition, the proper washing of the fluoride would be extremely difficult.

[4] S. L. Penfield and J. C. Minor, *Amer. J. Science* (3), **47**. 389, 1894; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **422**. 186, 1910; F. P. Treadwell and A. A. Koch, *Zeit. anal. Chem.*, **43**. 469, 1904. According to Treadwell and Koch (*l.c.*), the loss of calcium fluoride per 100 c.c. of wash-water is about 0·0015 grm. With a one-gram sample, therefore, from 0·04–0·05 per cent. of fluorine will entirely escape observation"—W. F. Hillebrand (*l.c.*).

$$\text{Amount of fluorine} = 0{\cdot}6543w;$$

and,

$$\text{Amount of calcium fluoride} = 1{\cdot}3447w.$$

In illustration,

Calcium fluoride (found)	0·0426 grm.
Calcium sulphate (found)	0·0724 grm.
Calcium sulphate (theory)	0·0743 grm.

No phosphates or silicates were present. Hence, it is assumed that the impurity was calcium sulphate not perfectly washed away. Consequently, the amount of fluorine in the 2-grm. sample is $0{\cdot}6543 \times (0{\cdot}0724 - 0{\cdot}0426) = 0{\cdot}0195$ grm. Hence, the sample has 0·98 per cent. of fluorine; or, 2·01 per cent. of calcium fluoride.

Errors.—Owing to the relatively small amounts of fluorine usually present in natural silicates, great care must be taken to prevent, as far as possible, any contamination of the calcium fluoride. The chief sources of error are: (1) loss of fluorides owing to the "adsorption" by the voluminous "silica" precipitates;[1] (2) the solubility of calcium fluoride in water and acetic acid; (3) loss of calcium fluoride by volatilisation, particularly in contact with the filter papers; and (4) the contamination of the precipitated calcium fluoride with phosphates, silica, calcium silicate, or calcium sulphate.

Correction of the Analysis "Total" for Fluorine.—In summing up the results of a silicate analysis which includes appreciable amounts of fluorine or chlorine, the sum of the constituents will exceed the limit "100 ± 0·5." This is due to the fact that the bases have been calculated as oxides when some of the bases were really present as fluorides or silicofluorides. For instance, a translucent white glass furnished on analysis:[2]

SiO_2.	Al_2O_3.	MnO.	ZnO.	MgO.	CaO.	Na_2O.	F.
64·8	9·3	1·1	7·0	0·2	1·9	10·8	8·1

The total reaches 103·2. But 38 grms. of fluorine are equivalent to 16 grms. of oxygen, or 1 grm. of fluorine is equivalent to 0·42105 grm. of oxygen. Consequently 8·1 grms. of fluorine are equivalent to $8{\cdot}1 \times 0{\cdot}421 = 3{\cdot}4$ grms. of oxygen. Hence, we append to the statement: "Total, 103·2," "less 3·4 per cent. of oxygen, corresponding with 8·1 per cent. of fluorine."

§ 329. The Determination of Silica in the Presence of Fluorides.

For reasons stated on page 172, the silica cannot be properly determined by the method of page 167 when fluorides are present, but it can be determined in the "by-products" of the fluorine determination, namely, the three precipitates indicated on pages 637 and 638. Each filter paper is spread on a watch-glass, and the precipitates rinsed into one evaporating basin with dilute hydrochloric acid. Ignite the filter papers separately, and add the ashes to the basin. Decompose the precipitates with hydrochloric acid, and evaporate to dryness on a water bath. The silica is recovered in the usual manner. The mercury volatilises on ignition. The alumina, titanic oxide, ferric oxide, magnesia, and lime[3] can be determined separately in another portion of the silicate decomposed by the hydrofluoric acid treatment, or in the filtrate from the silica.[1]

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[1] Hence, some recommend collecting the different "silica precipitates," igniting, and again treating the residue with sodium carbonate, ammonium carbonate, etc.

[2] "Alumina" in the analysis includes ferric oxide.

[3] In glazes, the lead, tin, etc., can be conveniently determined in a portion decomposed with sulphuric and hydrofluoric acids.

§ 330. The Gravimetric Determination of Fluorine as Potassium Fluosilicate.

In Carnot's process[2] for the determination of fluoride, the silicate is digested with sulphuric acid, and the silicon tetrafluoride is passed into an aqueous solution of potassium fluoride,[3] and finally weighed as potassium fluosilicate. Carnot's process is thus based upon older methods by Fresenius, and by Wöhler. The method gives good results with many of the natural fluorides used industrially, and also with slags and frits. All these are supposed to be decomposed by hot concentrated sulphuric acid. Daniel considers that methods depending on the volatilisation of silicon tetrafluoride are not reliable if amorphous silica, or silicates, be present, because a non-volatile fluoride may be formed which leads to low results. On the other hand, Classen[4] actually recommends: "One part of powdered quartz and 0·5 part of *precipitated silica* is to be intimately mixed in an agate mortar with the substance to be analysed." If there be any reason to suspect low results from the cause indicated by Daniel, the silicate can be treated as described in the preceding section. When all the silica has been separated, and the precipitate containing calcium fluoride and carbonate has been ignited, the mixture, if desired, can be treated by Carnot's process.

The Preparation of the Substance for Analysis.—Two grams of the substance under investigation are mixed with twice their own weight of finely ground, dry, quartz sand,[5] or rock crystal. If the sample contains other than about 0·1 grm. of fluorine, a proportionally less or greater amount than 2 grms. may be taken.[6]

Fitting up the Apparatus.—The mixture is placed in an Erlenmeyer's flask of about 150 or 250 c.c. capacity (*A*, fig. 200). The flask is closed with a three-hole rubber stopper, and connected with the system shown in the diagram. A Walter's gas-washing bottle[7] *C*, charged with concentrated sulphuric acid, is also fitted with a tube *B*, charged with soda lime. The former is connected with the flask containing the substance under investigation by means of a tube

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[1] H. Gilbert, *Corresp. Ver. anal. Chem.*, 3. 1, 1880. See R. Fresenius and E. Hintz (*Zeit. anal. Chem.*, 28. 324, 1889) for the determination of silica, etc., in cryolite; Loczka, *ib.*, 49. 328, 1910.

[2] A. Carnot, *Ann. Mines* (9), 3. 138, 1893; *Compt. Rend.*, 114. 750, 1892; *Bull. Soc. Chim.* (3), 9. 71, 1893; H. Lasne, *ib.* (2), 50. 167, 1888; *Ann. Chim. Anal.*, 2. 161, 182, 1897; E. Coutal, *ib.*, 2. 401, 1897; A. Liversidge, *Chem. News*, 24. 226, 1871; G. Harker, *ib.*, 82. 56, 64, 1900; J. Schuch, *Zeit. Landw. Vers. Wes. Öst.*, 9. 531, 1904; A. Küpffer, *Archiv Nat. Liv. Est. Kurlands.* (1), 5. 114, 1874; W. E. Burk, *Journ. Amer. Chem. Soc.*, 23. 825, 1901; P. Jannasch and A. Röntgen, *Zeit. anorg. Chem.*, 9. 267, 1895; K. Daniel, *ib.*, 38. 257, 1904; A. Hilemann, *ib.*, 51. 162, 1906; J. M. van Bemmelen, *ib.*, 15. 84, 1897; F. Bullnheimer, *Zeit. angew. Chem.*, 14. 101, 1901; E. Prost and F. Balthaser, *ib.*, 14. 292, 1901; *Bull. Assoc. Belg. Chim.*, 13. 453, 1899; H. von Kobell, *Journ. prakt. Chem.* (1), 92. 385, 1864; F. Stolba, *ib.* (1), 89. 129, 1863; F. Wöhler, *Pogg. Ann.*, 48. 87, 1839; J. Brandl, *Liebig's Ann.*, 213. 1, 1882; H. Schiff, *Liebig's Ann. Suppl.*, 4. 27, 1865; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1. 431, 1875; *Zeit. anal. Chem.*, 5. 190, 1866; S. Bein, *ib.*, 26. 733, 1887; E. Wrampelmeyer, *ib.*, 32. 550, 1893; J. Casares, *ib.*, 34. 546, 1895; 44. 729, 1905; A. Gautier and P. Clausmann, *Compt. Rend.*, 154. 1469, 1912; H. A. Weber, *Centr. Min.*, 2. 504, 1902.

[3] E. Deladrier (*Chem. Weekblad*, 1. 324, 1904) uses a solution of thorium chloride, and finally weighs the precipitated thorium fluosilicate.

[4] A. Classen, *Ausgewählte Methoden der analytischen Chemie*, Braunschweig, 2. 430, 1903.

[5] The quartz sand should be moistened with sulphuric acid, and calcined to remove organic matter, or treated by Hempel's process of purification (page 647).

[6] For example, 0·2 grm. of fluorspar or cryolite will suffice; 2 grms. of mineral phosphates containing from 2 to 3 per cent. of fluorine; and 5 grms. of bone ash with about 0·2 per cent. of fluorine can be taken for the analysis. If the silica and alumina are not to be determined, the preliminary treatment with Seemann's solution may not be needed. The ammonia must, however, be eliminated. If the fluorides are completely decomposed by sulphuric acid, the treatment with sodium carbonate may be omitted if the silica is not to be determined.

[7] J. Walter, *Dingler's Journ.*, 251. 367, 1884.

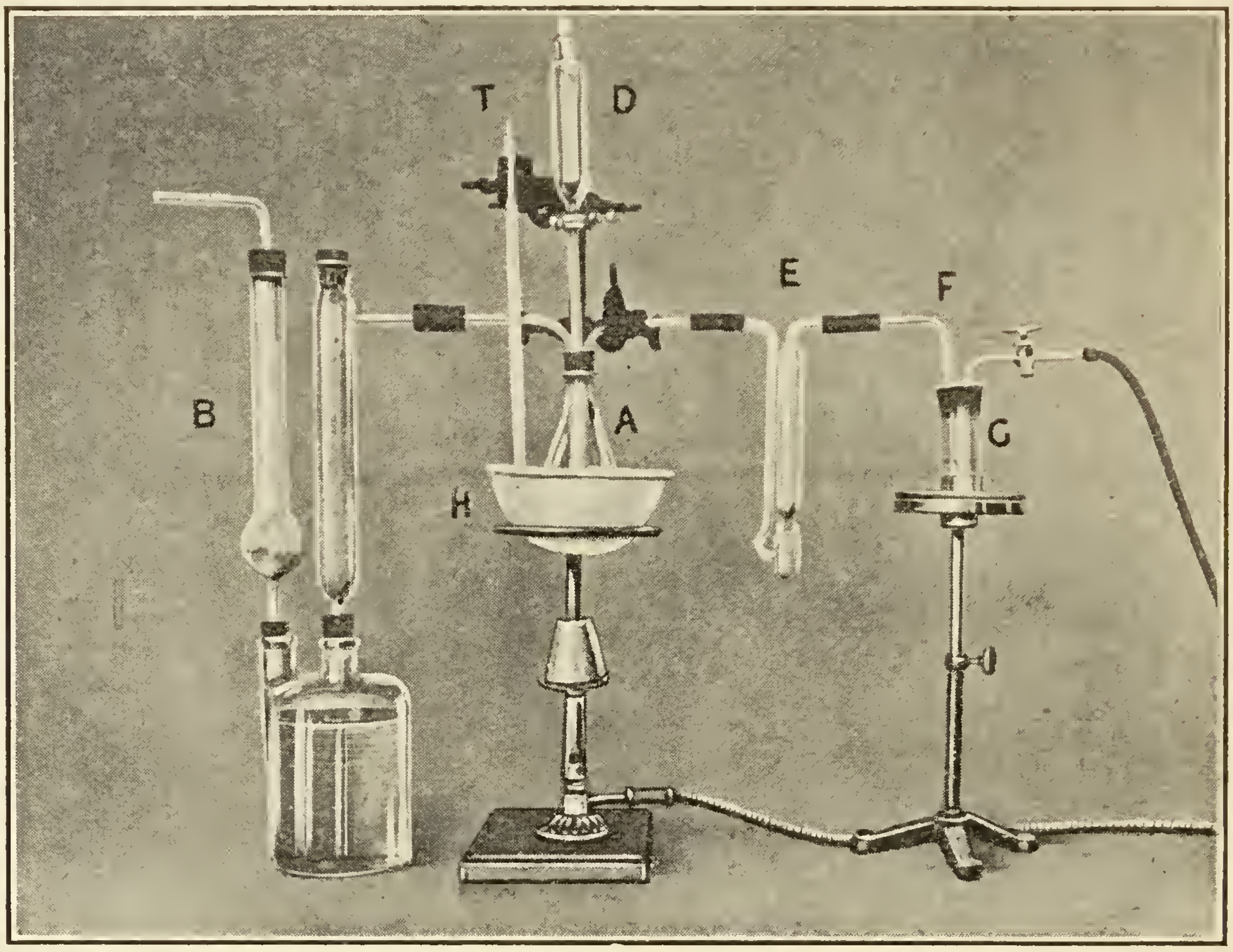

Fig. 200.—The determination of fluorine.

extending to the bottom of the Erlenmeyer's flask, *A*. The flask *A* is also fitted with a stoppered funnel *D*, leading to a von Babo's or similar drying tube *E*, packed with glass beads, in order to remove any acid vapours which might rise from the flask (*A*). The Emmerling's tube is connected with a tube (*F*) drawn out at one end. This dips 2 or 3 mm. beneath the surface of 10 c.c. of mercury contained in a small cylindrical vessel closed by a two-hole rubber stopper and fitted with a stoppered tube (*G*, fig. 201). This vessel is shown enlarged in the sectional diagram, fig. 202. This vessel also contains about 20 c.c. of a neutral solution of potassium fluoride [1]—20–25 per cent.

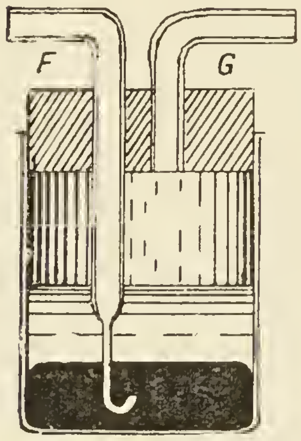

Fig. 201.—Decomposition Vessel.

The utmost care must be taken that all the glass parts between *B* and *G* be thoroughly dried. The drying is best effected by aspirating a current of dry air through the apparatus while the different parts are warmed.

The Decomposition of the Fluoride.—Add 40 c.c. of concentrated sulphuric acid [2] to the flask *A* by means of the funnel *D*. Aspirate a current of air through the system so that about one bubble per second rises through the mercury in *F*. The flask *A* is heated in a suitable oil bath, *H*, and the temperature gradually raised to 150° or 160° (*T* represents a thermometer). The fluorides in *A* commence to decompose at about 100°, and potassium fluosilicate begins to separate in the aqueous solution in *G*. If any bubbles of the fluosilicate stick to the walls of *G*, they must be broken up by gently rotating the fluid. When no new bubbles of the fluosilicate are formed, aspirate air a little more vigorously through the system for about half an hour.

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[1] Potassium Fluoride Solution.—Commercial potassium fluoride is generally acid and attacks glass. To prepare this for the work, dissolve 25 grms. in 80 c.c. of distilled water in a platinum dish; add dilute potash solution, drop by drop, until the solution is neutral to tincture of cochineal. Add absolute alcohol, drop by drop, until the solution shows a faint turbidity. Let the precipitate settle and filter. If the solution is free from potassium fluosilicate, it should give no precipitate when 10 c.c. is mixed with 40 c.c. of water and 50 c.c. alcohol (90 per cent.).

[2] The sulphuric acid should be free from oxides of nitrogen, and hydrochloric and hydrofluoric acids. This can be effected by heating the acid in a platinum basin along with a little powdered quartz.

The Preparation of the Potassium Fluosilicate for Weighing.—Decant, by means of a pipette, the fluid containing the clear gelatinous precipitate into an Erlenmeyer's flask; wash the absorption vessel (*G*) and the mercury two or three times with a little distilled water.[1] The main liquid and the washings are collected in the same flask, the contents of which should not exceed 100 c.c. Shake the liquid with its own volume of absolute alcohol; let the mixture stand 2–3 hours; decant the clear liquid through a Gooch's crucible which has been dried at 100° and weighed; wash the precipitate on to the filter with a mixture of equal volumes of water and alcohol, taking care to leave any globules of mercury in the flask; continue washing until the washings give no precipitate with calcium chloride—30–40 c.c. of the dilute alcohol are usually sufficient. Dry the Gooch's crucible and contents at 100°, and weigh.

Weighings.—A half-gram sample of purple Cornish stone, when treated as described above, furnished:

Crucible and precipitate	8·4519 grms.
Crucible alone	8·4321 grms.
Potassium fluosilicate	0·0198 grm.

The weight of the potassium fluosilicate, multiplied by 0·517, gives the corresponding amount of fluorine; and by 1·06245, the corresponding amount of calcium fluoride. Hence, the sample contained the equivalent of $0{\cdot}517 \times 0{\cdot}0198 = 0{\cdot}0102$ grm. or 2·04 per cent. of fluorine; or $1{\cdot}06245 \times 0{\cdot}0198 = 0{\cdot}0210$ grm. or 4·2 per cent. of calcium fluoride.

Disturbing Factors.—This method gives more exact results with less trouble in manipulation than by the precipitation process (page 637). The principal sources of error are: (1) The presence of moisture in the air or the tubes, etc., through which the silicon tetrafluoride passes. This causes a decomposition of the silicon fluoride before it reaches the potassium fluoride, and thus causes low results. (2) The passage of sulphuric acid fumes along with the gases from the flask *A*. This would decompose the potassium fluoride in the receiving vessel and lead to the formation of potassium fluosilicate, giving high results. (3) Incomplete decomposition of the fluoride in the flask *A*; and (4) the action of the potassium fluoride on the glass. To avoid the latter, Carnot recommends coating the surfaces of the flasks and tubes used in the determination with, say, copal resin.

A blank experiment will soon show whether the reagents and method are trustworthy. When *chlorides* are present, a U-tube containing pumice saturated with anhydrous copper sulphate (page 554) must be interposed between *E* and *F*. If the mercury in *G* has a greenish film towards the end of an experiment, *iodides* are probably present. If so, start a new experiment with a tube of copper turnings interposed, with the object of arresting the iodine. If *organic* matter be present, this should be removed by calcination at a low temperature; but since there is some danger of losing fluorine in the calcination, a tube of freshly calcined quicklime may be interposed between the copper sulphate tube and *G*. The calcium oxide tube for the organic matter must follow, not precede, the copper sulphate tube, since hydrogen chloride in contact with calcium oxide might form some water, which is fatal to the success of an experiment.

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[1] If the glass is attacked the experiment is vitiated. Some object to the use of the "policeman," since it removes silica from the glass. The silica is formed by the action of the fluorides.

Offermann's Volumetric Process.—Offermann[1] proceeds by the method of Carnot, just outlined, but he collects the silicon tetrafluoride in water, and titrates with $\frac{1}{10}$N-potash solution with cochineal as indicator: $3SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + Si(OH)_4$; and, $H_2SiF_6 + 6KOH \rightarrow 6KF + Si(OH)_4 + 2H_2O$. Hence, one molecule of potash—KOH—corresponds with an atom of fluorine—F. If phenolphthalein be used as indicator, the reaction is $H_2SiF_6 + 2KOH \rightarrow K_2SiF_6 + 2H_2O$.

§ 331. The Colorimetric Determination of Fluorine—Steiger's Process.

Steiger[2] has devised a process for the determination of fluorine which is based on the well-known fact that the presence of fluorine has a powerful bleaching effect upon the yellow colour produced when a solution of a titanium salt is peroxidised by hydrogen peroxide. In this process a known volume of the solution containing the fluorine is mixed with a known amount of titanium. The tint of this solution is compared in a colorimeter with a second solution containing an equivalent amount of titanium, and the bleaching effect is recorded. The extent of the bleaching enables the amount of fluorine to be computed as indicated below.

Preparation of the Solution.—Fuse 2 grms. of the powdered and dry sample—say Cornish stone—with 8 grms. of sodium carbonate, and extract the cold mass with hot water. Add 4 grms. of ammonium carbonate. Warm the mixture for a few minutes, and continue the heating on a water bath until the ammonium carbonate is destroyed,[3] and the volume of the liquid does not exceed 75 c.c.

Standard Solution.—Pipette 10 c.c. of the standard solution of titanium sulphate[4] into a 100-c.c. flask; add 4 c.c. of hydrogen peroxide and 3 c.c. of concentrated sulphuric acid. Make the solution up to the mark with water. 100 c.c. of this solution contain 0·01 grm. of TiO_2

Test Solution.—Add 3 or 4 c.c. of hydrogen peroxide to the 75 c.c. obtained during the evaporation of the solution containing the sample under investigation. Then add 10 c.c. of the standard titanium solution.[5] Add about 4 c.c. of concentrated sulphuric acid to neutralise the sodium carbonate in the solution.

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[1] H. Offermann, *Zeit. angew. Chem.*, **3**. 615, 1890; F. Stolba, *Journ. prakt. Chem.* (1), **89**. 129, 1863; *Zeit. anal. Chem.*, **2**. 396, 1863; J. Zellner, *Monats. Chem*, **18**. 749, 1897; T. Haga and Y. Osaka, *Chem. News*, **71**. 98, 1895; S. L. Penfield, *ib.*, **39**. 179, 1879; *Amer. Chem. Journ.*, **1**. 27, 1879; H. Gilbert, *Corresp. Ver. anal. Chem.*, **3**. 114, 1880; A. E. Haswell, *Rep. anal. Chem.*, **6**. 223, 1886; G. B. van Kampen, *Chem. Weekblad*, **8**. 856, 1911. S. Bein (*Rep. anal. Chem.*, **6**. 169, 1886) collects and weighs the precipitated silica.

[2] G. Steiger, *Journ. Amer. Chem. Soc.*, **30**. 219, 1908; H. E. Mervin, *Amer. J. Science* (4), **28**. 119, 1909. The intense reddish-brown colour furnished by titanic salts with dihydroxymaleic acid is also bleached by fluorine in an analogous way—H. J. H. Fenton, *Journ. Chem. Soc.*, **93**. 1064, 1908. A. Gautier and P. Clausmann (*Compt. Rend.*, **154**. 1670, 1753, 1912) separate the fluorine as lead fluoride, and the lead is subsequently determined colorimetrically (page 339).

[3] To prevent the formation of ammonium sulphate later on. Ammonium sulphate leads to high results, because it, like fluorine, bleaches the titanium solution.

[4] STANDARD TITANIUM SULPHATE.—Heat an intimate mixture of 1 grm. of titanium dioxide and 3 grms. of ammonium persulphate until the vigorous reaction has ceased. Drive off the ammonium persulphate by heat. Heat the residue with 20 c.c. of concentrated sulphuric acid (sp. gr. 1·84) until the acid fumes copiously. Pour the cold solution into 800 c.c. of water. The titanium oxide soon dissolves. Then add 57·5 c.c. of concentrated sulphuric acid, and make the solution up to a litre. The solution contains 0·001 grm. of TiO_2 and nearly 0·1 grm. of H_2SO_4 per c.c. Verify the result by a determination of the TiO_2 by one of the processes pages 203 *et seq.*

[5] The hydrogen peroxide prevents the precipitation of $Ti(OH)_4$ by the alkaline carbonates.

When the solution is neutral, it acquires a light orange tint. Add a drop or two of an aqueous solution of sodium carbonate to neutralise the acid and discharge the colour. Add a drop or two of sulphuric acid to restore the colour, and then add enough concentrated sulphuric acid[1] to make a 3–5 per cent. solution. Make the solution up to 100 c.c. The solution contains 0·01 grm.of TiO_2.

The Comparison.—These two solutions should have the same tint, because they have the same amount of titanium per c.c.; but if the test solution contains fluorine, it will have a paler tint owing to the bleaching effect of this element. The comparison can be made in Nessler's glasses—6 cm. long, 2·7 cm. diameter, placed over a white surface in diffused daylight. The comparison can also be made in a suitable colorimeter—say Duboscq's colorimeter. The depths of the liquids in the two tubes are adjusted so that when the tubes are changed right to left, and left to right, the tints appear the same, or the left one appears uniformly darker.[2] The ratio

$$\frac{\text{Depth of fluorine solution}}{\text{Depth of solution with no fluorine}} \times 100$$

is then noted. This number is taken as an abscissa, and the corresponding ordinate of the standard curve, fig. 202, represents the amount of fluorine in the two-gram sample. For instance, if the standard solution had a depth 4·41 cm., and the test solution 3·75 cm., the ratio is

$$\frac{3{\cdot}75}{4{\cdot}41} \times 100 = 85{\cdot}0\,.$$

The ordinate corresponding with the abscissa 85 is 0·00052. This latter number represents the amount of fluorine in the given sample. Supposing that 2 grms. of the sample be undergoing analysis, the sample would be reported to contain 0·026 per cent. of fluorine.

The Standard Bleaching Curve.—A standard solution of sodium fluoride is prepared from recrystallised, washed, and strongly ignited, pure sodium fluoride by dissolving 2·21 grms. of sodium fluoride in a litre of water. 1 c.c. of this solution is equivalent to 0·001 grm. of fluorine. A series of comparisons are made with solu-

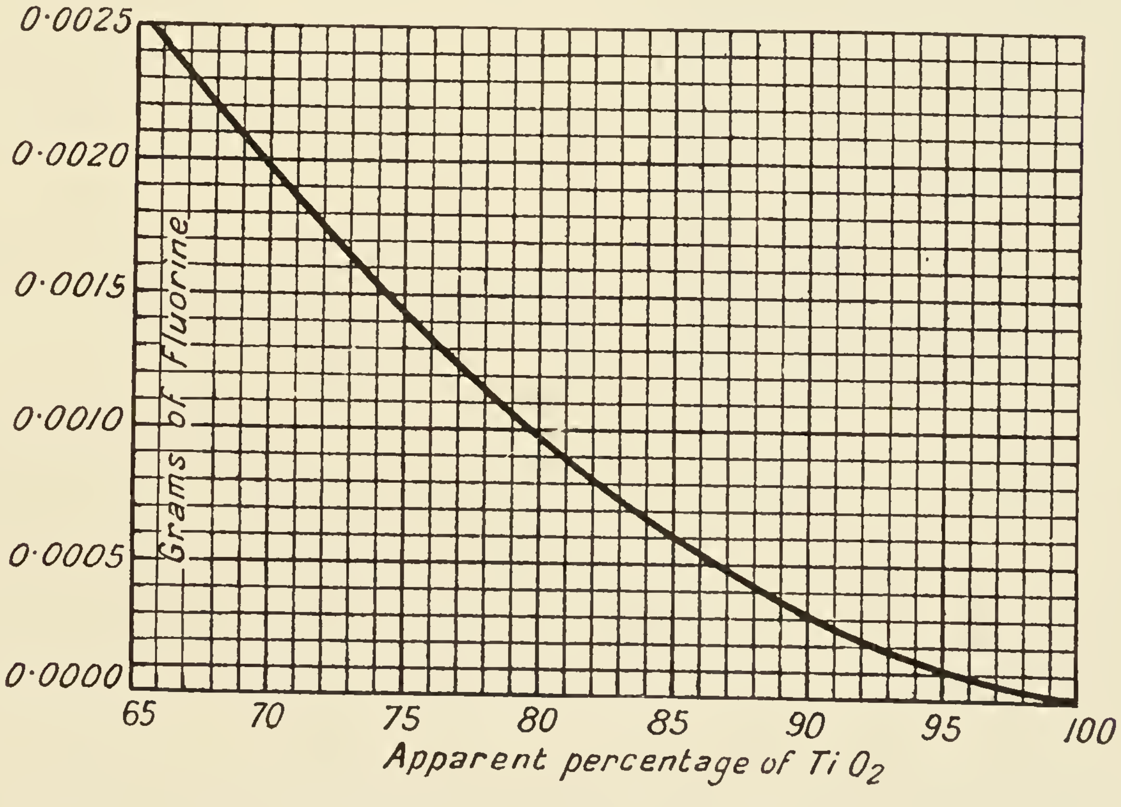

Fig. 202.—Steiger's standard bleaching curve.

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[1] That is, about 5 c.c. of the concentrated sulphuric acid per 100 c.c. of solution.

[2] Since the left eye is usually more sensitive to the tint.

tions containing 4 c.c. of hydrogen peroxide and 3 c.c. of concentrated sulphuric acid, against similar solutions containing no fluoride. In this manner, a curve similar to that shown in fig. 202 is obtained. It was found that with

Fluorine . . .	0·0005	0·0010	0·0015	0·0020	0·0025	grm.
Titanium . . .	86·41	79·24	74·67	69·60	66·40	grms.

The numbers in the last line represent the apparent amounts of titanium measured in terms of the ratio

$$\frac{\text{Depth of liquid containing fluorine}}{\text{Depth of liquid free from fluorine}} \times 100 .$$

Errors.—The method is not satisfactory when the amount of fluorine exceeds 0·125 per cent., that is, 0·0025 grm. on a two-gram sample. If more fluorine be present, the amount of the sample taken must be lessened. If the temperature deviates appreciably from the temperature prevailing at the time the standard bleaching curve was made, the tint of the solution will appear paler, and high results will be obtained. Sodium and potassium sulphates in large amounts have a bleaching effect, but, if a large excess of sulphuric acid be present, the effect is not well marked. Aluminium sulphate intensifies the colour and thus gives low results. Quantities of silica less than 0·1 grm. have but little influence on the result. The method of preparing the sample for comparison eliminates most of the silica and alumina, and what remains has practically no influence on the result. Phosphoric acid bleaches the solution like fluorine, but the amount usually present in silicates does no harm. The tints are dependent on the proportion of sulphuric acid in the solution, and it is very important to adjust the solutions undergoing comparison so that they contain approximately the same proportion of sulphuric acid, both in making up the solutions for the standard bleaching curve, and in making the tests. According to Blum,[1] when but "little acid is present, the colours cannot be properly matched. This is the case, for instance, with 0·003 grm. fluorine in 2 per cent. sulphuric acid solutions; but with 10 per cent. of sulphuric acid a fairly satisfactory comparison was possible with as much as 0·005 grm. of fluorine." As a result of his investigation, Merwin states that an "accuracy of 0·0002 grm. may be expected. The probable error is therefore not half as great as with standard gravimetric methods."

§ 332. The Determination of Fluorine as Gaseous Silicon Fluoride—Oettel and Hempel's Process.

The simplest method for the determination of fluorine in silicates decomposable by sulphuric acid, and exact enough for commercial requirements, is to treat the substance with concentrated sulphuric acid, and to measure the volume of the gaseous silicon fluoride evolved during the reaction. Oettel, and Hempel and Schleffler,[2] have devised special instruments—called fluorometers—for this purpose. Oettel's fluorometer is illustrated in fig. 203.

Charging the Apparatus.—It consists of a decomposition flask *A* (about 100 c.c.), a (150–180 c.c.) burette *B*, and a levelling tube *C*. The burette is filled with dry mercury, which is brought to zero by means of the levelling tube *C*. The thick-walled rubber tube connecting the levelling tube with the burette is then clamped. From $\frac{1}{4}$ to $\frac{1}{2}$ c.c. of concentrated sulphuric acid[1] is poured on to the surface of the mercury. The decomposition flask must be perfectly dry. Transfer to the dry flask 0·3 to 0·5 grm. of finely powdered cryolite (or fluorspar) intimately mixed with twenty times its weight of calcined quartz.[2]

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[1] W. Blum, *Bull. U.S. Geol. Sur.*, **422**. 192, 1910.

[2] F. Oettel, *Zeit. anal. Chem.*, **25**. 505, 1886; W. Hempel and W. Scheffler, *Zeit. anorg. Chem.*, **20**. 1, 1899; W. E. Burk, *Journ. Amer. Chem. Soc.*, **23**. 824, 1901; J. Shuch, *Zeit. Landw. Vers. West. Oest.*, **9**. 531, 1904; O. R. Böhm, *Oestr. Chem. Ztg.*, **10**. 61, 1907; A. Jodlbauer, *Zeit. Biol.*, **44**. 259, 1903; H. Wislicenus, *Zeit. agnew. Chem.*, **14**. 706, 1901; Treadwell and Koch, *l.c.*

Evolution of the Gas.—Place the flask on the burette in the position shown in the diagram. Let the whole apparatus stand 15 minutes to assume the temperature of the room. Add 50 c.c. of concentrated sulphuric acid to the flask by means of a pipette.[3] Insert the stopper and fill the cup with mercury so as to seal the joint. The 100-c.c. bulb *A* will now be about half full. Open the clamp to connect the burette with the levelling tube. The pressure of the air is reduced by the descent of the mercury. Read the thermometer and barometer. Heat the flask by means of a small flame until the sulphuric acid begins to boil. This should take about 20 minutes. In another 10 minutes the reaction will be complete. Raise or lower the levelling tube so as to keep the level of mercury some 10 to 15 cm. lower than the level in the burette. Shake the flask from time to time as much as possible by moving the whole stand, but without jerking the mercury from the mercury-sealed joints. Let the flask cool for about 2 hours, when it will no doubt have attained the temperature of the room. Raise the levelling tube from time to time during the cooling to counterbalance the diminished pressure of the cooling gas. Level the mercury in the bulb and levelling tube. Read the burette, thermometer, and barometer. Suppose the following results have been obtained :—

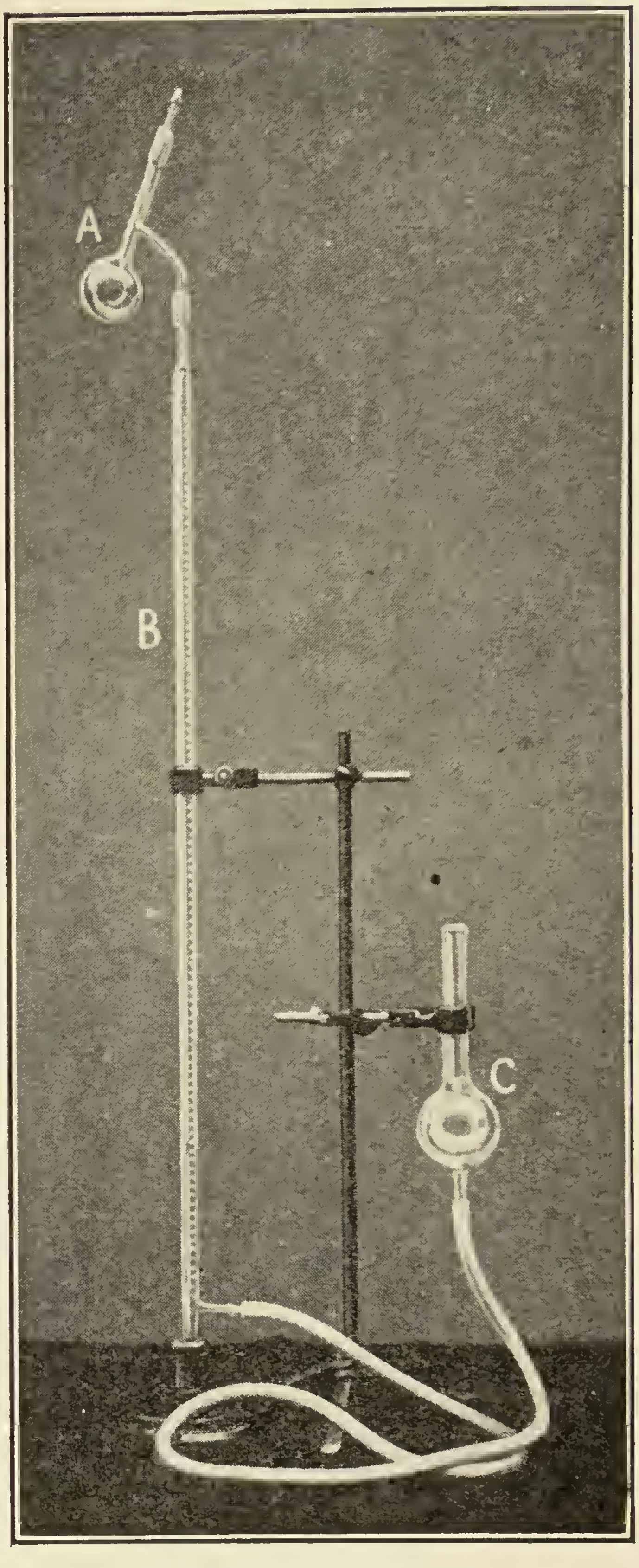

Fig. 203.—Oettel's fluorometer.

Readings and Calculations.—Weight of cryolite, 0·5261 grm. Temperature, t_0, at the beginning, 17° ; barometer at the beginning, 7·754 mm. ; temperature, t_1, at the end, 18° ; barometer at the end, 757·4. Vapour pressure of the concentrated sulphuric acid at this temperature is equivalent to 5·4 mm. mercury.

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[1] "The concentrated sulphuric acid used in the work is made by heating the concentrated acid of the laboratory in a porcelain dish with flowers of sulphur. The acid is then poured off from the molten sulphur, and evaporated down to two-thirds its volume." W. Hempel, *Methods of Gas Analysis*, London, 322, 1892.

[2] "The silicon dioxide required is best obtained by pulverising rock crystal and igniting the powder in a combustion tube in a current of oxygen." W. Hempel, *l.c.* ; see also page 641. P. Drawe (*Zeit. angew. Chem.*, 25. 1371, 1912) uses 0·5–0·6 of felspar (instead of quartz) along with 5 grms. of anhydrous copper sulphate (page 554) to make sure that the moisture is removed.

[3] Do not touch the flask needlessly, or it may be warmed and cause an expansion of the gas.

Hence the observed pressures of the gas at the beginning, p_0, and at the end, p_1, are respectively 757·4 – 5·4 = 752 mm. The observed volume of the gas is 85·9 c.c. By means of the well-known formula,

$$\text{Volume at } t_0 \text{ and } p_0 = \text{ volume at } t_1 \text{ and } p_1 \times \frac{p_1(273 + t_0)}{p_0(273 + t_1)},$$

it follows that the volume of the gas at 18°, 752 mm. pressure, is 85·9 c.c.; volume of the gas at 17°, 752 mm. pressure, is 85·6 c.c.; volume of the gas at 0°, 760 mm. pressure, is 79 6 c.c. But 50 c.c. of sulphuric acid absorb very nearly 1·4 c.c. of silicon fluoride; hence, 79·6 + 1·4 = 81 c.c. of SiF_4 were produced during the reaction. But 1 c.c. of silicon fluoride at 0° and 760 mm. pressure represents 0·003436 grm. of fluorine. Hence, 81 c.c. represents 0·2814 grm. of fluorine per 0·5261 grm. of cryolite; or the cryolite has 53·49 per cent. of fluorine.

In illustration of the accuracy of the process, Oettel quotes the following results with calcium fluoride:

Found . . .	0·2183	0·2349	0·1051	0·2792	0·2776	grm.
Calculated. . .	0·2173	0·2350	0·1050	0·2801	0·2782	grm.

This is all that can be desired in commercial work. To get accurate results, it is highly important to exclude all traces of moisture from the generating apparatus.[1]

§ 333. The Analysis of Calcium Fluoride—Fluorspar.

The preceding process may be employed for all silicates which are completely decomposed by sulphuric acid, as indicated on page 646. Hence, calcium fluoride is easily treated by the process. In commercial analyses of fluorspar, calcium fluoride, silica, and calcium carbonate are usually determined. In special cases the amount of lead, iron, zinc, sulphur, and barium sulphate may be required. One rapid process is as follows:—

1. *Calcium Carbonate.*—Heat 2 grms. of the dried (110°) material until it has constant weight. The loss in weight represents carbon dioxide. This amount of carbon dioxide, multiplied by 2·2748, represents the calcium carbonate.[2]

2. *Silica.*—Stahl[3] determines the silica in fluorspar by evaporating 2 grms. of the powdered and dry mineral (110°) to dryness with 4 c.c. of hydrofluoric acid in a platinum dish, and repeating the operation twice with 2 c.c. of hydrofluoric acid. Add a few drops of hydrofluoric acid and a few drops of ammonium hydroxide to precipitate the iron. The residue is evaporated to dryness and

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[1] P. Drawe (*Zeit. angew. Chem.*, 25. 1371, 1912).

[2] W. J. Waring, *Chem. Eng.*, 4. 23, 1906; *ib.*, 3. 65, 1905; L. Westerburg, *Chem. Ztg.*, 26. 967, 1902; A. W. Gregory, *Chem. News*, 92. 184, 1905. For the complete analysis, the calcium fluoride is mixed with a known amount of powdered rock crystal, and the method of page 637 applied. Due allowance is made for the silica purposely added.

Calcium carbonate is sometimes determined by digesting, say, 1 gram of the finely powdered sample with 10 c.c. of a 10 per cent. solution of acetic acid for about an hour on a water bath. The mixture is filtered through an ashless filter paper, washed about four times with water, and the filter paper "ashed" at as low a temperature as possible. The loss in weight would represent the amount of calcium carbonate in the given sample, were it not for the fact that calcium fluoride is slightly soluble in acetic acid. E. Bidtel (*Journ. Ind. Eng. Chem.*, 4. 201, 1912) says that, in using this method with clean crystals of fluorspar, 0·0015 grm. is dissolved. Hence, if

Weight of original sample	1·0000	grm.
Weight after treatment with acetic acid	0·9910	grm.
Loss	0·0090	grm.
Loss due to CaF_2 dissolved	0·0015	grm.
Calcium carbonate	0·0105	grm.

[3] K. F. Stahl, *Journ. Amer. Chem. Soc.*, 18. 415, 1896.

ignited at a dull red heat to constant weight.[1] The loss in weight represents the silica. To correct for the calcium carbonate, multiply the amount of carbon dioxide by 0·5000 to get the corresponding decrease in weight due to the change from calcium carbonate to calcium fluoride. This result is added on to the silica just determined to get the "total silica."[2]

3. *Calcium Fluoride.*—Mix 1 grm. of the powdered and dry (110°) material with sulphuric acid to form a "pasty" mass.[3] Heat the mixture over the Bunsen's burner, gradually raising the temperature, until all the sulphuric acid is expelled, and the mass is dry, and the weight constant. It is assumed that all the calcium is transformed into sulphate. Cool and weigh. Multiply the amount of carbon dioxide by 0·82 to get the corresponding gain in weight due to the change of the calcium carbonate to calcium sulphate. Subtract this number, and add that obtained for the silica to the result. The gain in weight due to the change of the calcium fluoride to calcium sulphate so obtained, multiplied by 1·3448, represents the amount of calcium fluoride.[4]

Calculations and Weighings—The following weighings and calculations illustrate the method of working:

Dish with 2 grms. sample before ignition	28·4491	grms.
Dish with 2 grms. sample after ignition	28·4440	grms.
Carbon dioxide	0·0051	grm.
Calcium carbonate (0·0051 × 2·2748)	0·0116	grm.
Loss due to change from carbonate to fluorine (0·0051 × 0·5)	0·0025	grm.
Gain due to change from carbonate to sulphate (0·0051 × 0·82)	0·0042	grm.
Dish (2 grms. sample) before HF treatment	28·4491	grms.
Dish (2 grms. sample) after HF treatment	28·4443	grms.
Silica and change from carbonate to fluoride	0·0048	grm.
Loss on change from carbonate to fluoride	0·0025	grm.
Silica	0·0073	grm.
Dish (2 grms. sample) before H_2SO_4 treatment	28·4491	grms.
Dish (2 grms. sample) after H_2SO_4 treatment	29·9152	grms.
Gain on change fluoride and carbonate to sulphate	1·4661	grms.
Gain on change of carbonate to sulphate	0·0042	grm.
Silica lost and change fluoride to sulphate	1·4619	grms.
Silica lost	0·0073	grm.
Gain from change fluoride to sulphate	1·4692	grms.
Calcium fluoride (1·4692 × 1·3448)	1·9754	grms.

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[1] Bidtel (*l.c.*) mixes the powdered fluorspar in the platinum crucible with an emulsion of 1 gram of yellow mercuric oxide in water; evaporating to dryness; heating to a dull red heat; cooling and weighing. The object of this treatment is to oxidise certain sulphides to sulphates, *e.g.*, $PbS + 4HgO = 4Hg + PbSO_4$. The residue is then treated for silica with hydrofluoric acid.

[2] If alumina or silicates be present, the result is not quite correct.

[3] Instead of using this process, the residue left after the treatment removing calcium carbonate by acetic acid (page 648) may be employed, and there is then no need to introduce a correction for calcium carbonate.

[4] The calcium sulphate can be fused with about 10 grms. of sodium carbonate, and digested in a slight excess of hydrochloric acid. Any barium sulphate present will remain insoluble. This is F. Wöhler's process (*Pogg. Ann.*, 48. 87, 1839). See also R. F. Weinland and J. Alfa, *Zeit. anorg. Chem.*, **21**. 45, 1899; K. Daniel, *ib.*, **38**. 257, 1904; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, I. 435, 1875. For barium and sulphur in fluorspar by fusion in a bomb with Parr's fusion mixture, see H. G. Martin, *Journ. Ind. Eng. Chem.*, I. 462, 1909.

Consequently, the sample contained approximately 0·6 per cent. of calcium carbonate; 0·4 per cent. of silica; and 98·8 per cent. of calcium fluoride.[1]

§ 334. The Analysis of Sodium Silicofluoride.

The fluorine cannot be determined as silicon fluoride, because, on treatment with acids, the silicon fluoride is accompanied by hydrogen fluoride, which etches glass. Thus, with concentrated sulphuric acid,

$$Na_2SiF_6 + H_2SO_4 \rightarrow Na_2SO_4 + SiF_4 + 2HF.$$

Hence, on heating a known weight of the substance with concentrated sulphuric acid in a platinum dish, until the white fumes of sulphuric acid are given off, sodium sulphate and sulphates of the other bases present will remain.[2] The bases can be determined in the usual manner. Sodium silicofluoride can be titrated with N sodium hydroxide, using phenolphthalein as indicator. The reaction is represented:

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + H_2O.$$

Commercial samples contain about 95 per cent. of sodium silicofluoride.

The loss on ignition of sodium silicofluoride does not represent the "water" because, on heating, this salt decomposes into sodium fluoride and silicon fluoride: $Na_2SiF_6 \rightarrow 2NaF + SiF_4$. To determine the water, use the method indicated on page 572, namely, fusion in glass tubes with lead oxide.[3]

Hydrofluosilicic acid is a by-product in the manufacture of artificial manures. The acid is treated with soda or common salt in order to precipitate sodium silicofluoride. Hence the commercial salt may be contaminated with chlorides, which can be determined as described below.

§ 335. The Properties of Silver Chloride.

Chlorides are determined by adding a solution of silver nitrate to an acidified solution of the chloride. The white curdy[4] precipitate of silver chloride is washed, dried, and weighed. In 1857, Mulder[5] pointed out that the solubility of silver chloride in the mother liquid is sufficient to disturb all quantitative analyses based upon the precipitation of silver chloride, and Cooke[1] considered that about 0·0001 grm. of silver chloride is dissolved per 100 c.c. of liquid used in washing. It is now considered to be a well-established fact that freshly precipitated silver chloride is soluble in water to the extent of about 0·000154 grm. per 100 c.c. at 21°, and 0·00217 grm. at 100°.[2] The solubility of freshly precipitated silver chloride steadily diminishes to about a milligram per litre when the precipitate is left standing in contact with the mother liquid. This change in the solubility is generally supposed to be due to the fact that the solubility of many salts, which are only slightly soluble in water, is affected by the size of the grain. The smaller the grain, the greater the solubility.[3] Silver chloride when first precipitated is in a very finely divided condition, and the small grains grow into larger grains at the expense of the very smallest granules, on long standing. The solution is also generally warmed, so as to coagulate any colloidal silver chloride which may be formed, and so prevent a turbid filtrate passing through the filter paper.

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[1] Instead of using a separate portion of the sample, the residue from the silica determination may be mixed with 4 c.c. of hydrofluoric acid and a few drops of nitric acid. Cover the crucible with a lid and keep the mass warm for about half an hour. Then evaporate to dryness. The contents of the crucible should be white. If the contents of the crucible are not white, the iron oxide is converted into fluoride by the addition of a few drops of hydrofluoric acid. The iron, zinc, and lead fluorides are then extracted by the addition of 10 c.c. of a solution of ammonium acetate. The mixture is digested on a water bath for half an hour. Filter, and wash by decantation with hot water containing a little ammonium acetate solution, and finally with hot water. Ignite, and weigh as calcium fluoride. This can be verified by converting the fluoride into sulphate. The ammonium acetate solution is made by neutralising 400 c.c. of 80 per cent. acetic acid with ammonium hydroxide, adding 20 grms. of citric acid, and making the solution up to a litre with concentrated aqueous ammonia. About 0·0012 grm. CaF_2 per gram of fluorspar is lost by the ammonium acetate treatment.

[2] For the direct determination of silica and fluorine, use the process indicated on page 637. For the transformation into chlorides, use hydrochloric acid (1 acid, 2 water by volume)—F. Stolba, *Chem. Centr.* (3), **11**. 595, 1880.

[3] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**. 667, 1851; P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 357, 1904; E. Hintz and H. Weber, *Zeit. anal. Chem.*, **30**. 30, 1891.

[4] If but small quantities of silver chloride be present, the solution only becomes turbid. The suspended particles then settle very slowly.

[5] G. J. Mulder, *Die Silberprobirmethoden*, Leipzig, **19**. 311, 1859; *Chem. News*, **4**. 99, 125, 137, 204, 231, 297, 321, 1861; **5**. 2, 1862.

The presence of a small excess of either silver nitrate or sodium chloride reduces the solubility of the precipitated chloride.[4] A large excess of hydrochloric acid, alkaline chlorides or nitrates, metallic chlorides, or of silver nitrate augments the solubility of silver chloride. Thus, the solubility of silver chloride in different strengths of hydrochloric acid at 21° is, according to Whitby, as follows:

Hydrochloric acid . . .	0	1	5	10	per cent.
Silver chloride . . .	0·00154	0·0002	0·0033	0·0555	grm. per litre.

The lower solubility of silver iodide and bromide has led to the use of soluble iodides and bromides in place of chlorides for precipitating silver from solutions (page 333). The solubilities of the three halides in water at 20° are:

AgCl.	AgBr.	AgI.
0·00154	0·000084	0·0000028

The silver chloride during precipitation is inclined to carry down, or "occlude" or "adsorb," silver nitrate[5] and sodium chloride. These substances are associated in some way with the precipitated chloride, so that the impurities are not removed by washing. In general, the longer the precipitate remains in contact with the mother liquid, the greater the difficulty in removing the adsorbed salts. Precipitates formed in dilute solutions are generally more amenable to washing than precipitates formed in concentrated solutions.

White silver chloride dries (in the dark) to a white pulverulent mass which becomes yellow when heated. Silver chloride fuses at 260° to a transparent yellow liquid which attacks platinum very rapidly. At a high temperature, silver chloride commences to volatilise. When the molten mass is cooled, it forms a colourless or pale yellow mass. Silver chloride is easily reduced to the metal when heated in contact with organic matter, and hence the difficulty in getting rid of the filter paper used in separating the precipitate from the mother liquid.

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[1] J. P. Cooke, *Amer. J. Science* (3), **21.** 220, 1881; *Chem. News*, **44.** 234, 1881; D. Lindo, *ib.*, **45.** 193, 1882.

[2] A. F. Holleman, *Zeit. phys. Chem.*, **12.** 132, 1893; F. Kohlrausch and F. Rose, *ib.*, **12.** 234, 1893; F. Kohlrausch, *ib.*, **50.** 355, 1905; W. Böttger, *ib.*, **46.** 325, 1903; **56.** 83, 1906; T. W. Richards, *Zeit. anorg. Chem.*, **6.** 108, 1894; F. Field, *Chem. News*, **3.** 17, 1861; G. S. Whitby, *Ber. Internat. Congress App. Chem.*, **7.** 12, 1910; W. Böttger, *Zeit. angew. Chem.*, **25.** 1992, 1912.

[3] W. H. Wollaston, *Phil. Trans.*, **103.** 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, **34.** 495, 1900; G. Hulett, *ib.*, **37.** 385, 1901; **47.** 357, 1904.

[4] C. Hoitsema, *Zeit. phys. Chem.*, **20.** 272, 1896.

[5] J. S. Stas, *Œuvres Complètes*, Bruxelles, **1.** 337, 1894.

§ 336. The Gravimetric Determination of Chlorides.

The silicate is fused with sodium carbonate,[1] as described for the determination of sulphur (page 617). The clear aqueous solution of the fused mass, or an aliquot portion of the aqueous solution, is acidified with nitric acid in the cold.[2] Heat the solution to about 60°. Gradually add, with constant stirring,[3] about 5 c.c. of an aqueous solution of silver nitrate.[4] When the precipitate has settled, add a few more drops of the silver nitrate solution, and if a precipitate be formed, more silver nitrate must be added. When the addition of silver nitrate no longer produces a precipitate, heat the mixture to 60°,[5] and let the mixture settle in the dark,[6] say, overnight. Decant the cold solution through a (7·5-cm.) filter paper. Wash by decantation a few times with water just acidified with nitric acid. Transfer the precipitate to a filter paper,[7] and wash with acidulated water until a drop of the filtrate gives no turbidity with hydrochloric acid. Dry the precipitate between 90° and 95°, and separate it from the paper. Preserve the precipitate in a covered watch-glass. Incinerate the paper in a small weighed porcelain crucible—not platinum. Do not allow the paper to burn with a flame. When the carbon has disappeared, the chloride will be reduced to metal. Add a few drops of nitric acid, and warm the crucible, to dissolve the metallic silver; add a few drops of hydrochloric acid; evaporate the solution to dryness; and then transfer the precipitate in the watch-glass to the crucible. Heat the crucible and contents gently to about 180°, but not sufficiently high to fuse the silver chloride (260°). Cool, and weigh as silver chloride. If the silver chloride so obtained is quite soluble in ammonia, the work is finished; if an insoluble residue remains, proceed as follows:—

Purification of the Silver Chloride Precipitate.—In order to purify the precipitate from silica, alumina, etc., if any should be present, dissolve the precipitate in the crucible in aqueous ammonia; filter the solution to separate the insoluble residue; wash the residue with ammonia; acidify the solution with nitric acid; add a drop of silver nitrate; filter and wash the precipitated silver chloride as before. This precipitate can be collected on filter paper, but a Gooch's crucible with ignited asbestos is preferable. See page 430.

Calculations.—The weight of the silver chloride multiplied by 0·24738 represents the corresponding amount of chlorine. The sum of the different constituents in a silicate analysis may exceed the limit 100 ± 0·5 if appreciable amounts of chlorine be present, because some of the chlorine will have been reckoned as oxygen in evaluating the bases, etc. By the same process of reasoning as was employed for fluorine, every *n* per cent. of chlorine obtained must be multiplied by 0·2256 in order to get the equivalent amount of oxygen, and the product is appended to the analysis in this form: "Less *x* per cent. of oxygen, equivalent to *n* per cent. of chlorine."

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[1] All the reagents should be tested for possible and probable contamination with chlorides.

[2] H. S. Washington (*Manual of the Chemical Analysis of Rocks*, New York, 160, 1904) prefers to decompose the silicate with a mixture of nitric and hydrofluoric acids (free from chlorides) in a platinum basin; boil for an hour; filter through a platinum or rubber funnel into a platinum basin; and precipitate the silver chloride in the presence of an excess of nitric acid.

[3] So as to reduce as much as possible the adsorption of salts by the precipitate.

[4] Silver Nitrate Solution.—Dissolve 3·4 grms. of silver nitrate in 100 c.c. of water ($\frac{1}{5}$E).

[5] E. Alefeld (*Zeit. anal. Chem.*, **48.** 79, 1909) adds 5 c.c. of ether to the solution before adding silver nitrate, in order to coagulate the precipitate. Gooch's crucible (packed with asbestos) is used for the filtration. It is moistened with ether before the suction is applied. The filtration may here be done immediately after the precipitation. The precipitate is washed with water. M. Whittel (*Chem. Ztg.*, **7.** 559, 1884) recommends a drop of chloroform to coagulate the precipitate.

[6] White silver chloride soon becomes violet and finally dark brown, almost black, when exposed to the light. Some claim that there is then an appreciable loss, possibly owing to the formation of a sub-chloride. G. J. Mulder, *Die Silberprobirmethoden*, Leipzig, 59, 1859.

[7] If any chloride sticks tenaciously to the beaker, dissolve it in ammonia, transfer the solution to a weighed crucible, acidify with nitric acid, evaporate to dryness, dry at 150°, and weigh. Add the weight to the main mass of silver chloride.

Jannasch's Filter Tube.—Instead of using a Gooch's crucible, the stoppered tube as recommended by Jannasch[1] may be employed—fig. 204. This is fitted with a layer of glass-wool, from 0·5 to 1·0 cm. thick, in the neck, *B*; above this is a layer, *C*, of asbestos such as is used for the Gooch's crucible, 0·5 to 1·0 cm. thick. The narrow end of the tube is fitted into the filtration flask by means of a one-hole rubber stopper, fig. 49. Water is run through the tube until any particles of loose glass-wool have all been washed into the flask. Dry the tube for two or three hours at 150°, and when cold (50°–60°) insert the stopper *A*, and cool in a desiccator. Insert the stopper *D*, and weigh. Filter the silver chloride precipitate through the tube, and dry at 180°–200°, as indicated above. Insert the stoppers as before, and weigh. The increase in weight represents the silver chloride.

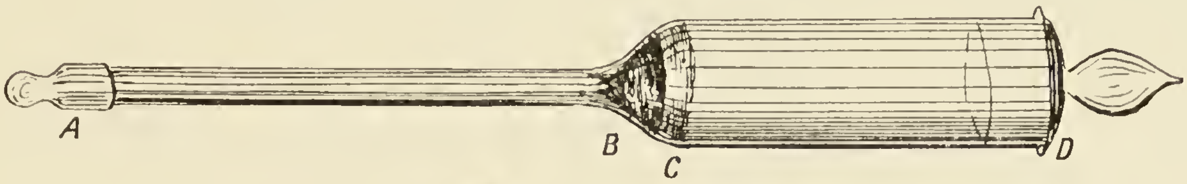

Fig. 204.—Jannasch's filter and weighing tube.

The Determination of Soluble Chlorides in Clays.—The chlorine present in the soluble salts in clays can be determined gravimetrically as just described; or volumetrically,[2] as indicated on pages 76 and 79; or by the turbidity method. The turbidity method is conducted in a similar manner to the turbidity process (page 631) for the determination of sulphates.[3] A solution of silver nitrate must be substituted for barium chloride; and sodium chloride substituted for calcium sulphate.

§ 337. The Determination of Silver.

The determination of silver is a reciprocal process to the determination of chlorides. In the latter case a silver salt is added to the soluble chloride; and in the former case a soluble chloride is added to the solution containing silver.[4] In each determination the precipitated silver chloride is prepared for weighing in the same way. The weight of the silver chloride multiplied by 0·7526 gives the corresponding amount of silver.

Benedickt and Gans' Gravimetric Process.[5]—Add an excess of potassium iodide to a solution containing an excess of about 10 c.c. dilute nitric acid.[6] Any silver present is precipitated as silver iodide. If too great an excess of potassium iodide be added, some silver iodide may remain in solution. The solution is then heated. If any lead be present, the precipitated lead iodide will be decomposed by this treatment, soluble lead nitrate will be formed, and iodine will be set free. The latter is volatilised. When the solution is free from the colour of iodine, the silver iodide is filtered off, washed, and weighed as in the case of silver chloride. The weight of silver iodide multiplied by 0·4594 gives the corresponding amount of silver. Hampe considers this "the most accurate of the wet processes for the determination of silver." It can be used for estimating the amount of silver in lead compounds.

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[1] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 11, 1904. Neither Jannasch's tube nor the Gooch's crucible is employed for collecting the first precipitate if the silver chloride is to be freed from silica.

[2] F. Muck (*Zeit. anal. Chem.*, **22**. 222, 1883), in the presence of organic matter, evaporates the fluid to dryness and moistens the residue with a solution of potassium or sodium hydroxide free from chlorine. Then warm the mass with chlorine-free potassium permanganate until the colour of the permanganate remains green. A drop of alcohol will destroy the green colour. Filter and wash. The chlorine is determined in the filtrate in the usual manner.

[3] T. W. Richards, *Internat. Cong. App. Chem.*, **8**. i, 423, 1913; P. A. Guye, *Journ. Chim. Phys.*, **10**. 145, 1913; F. Meyer and A. Stahler, *Zeit. anorg. Chem.*, **77**. 255, 1913.

[4] It appears to be advantageous to precipitate the silver by the addition of a soluble bromide, since silver bromide is less soluble than silver chloride; and still more advantageous to precipitate the silver as silver iodide, since this salt is even less soluble than silver bromide.

[5] R. Benedickt and L. Gans, *Chem. Ztg.*, **16**. 4, 12, 44, 1892; W. Hampe, *ib.*, **18**. 1899, 1894.

[6] If antimony be present, the addition of tartaric acid prevents its contaminating the precipitated silver iodide.

For the volumetric processes for silver, *vide* pages 76 and 79; for the cupellation process, page 326; and for metallic precipitation with cadmium or zinc,[1] follow the method of page 307.

Whitby's Colorimetric Process.[2]—This process is based on the development of a brown or yellow colour when a solution of a silver salt is heated with a little sodium hydroxide and an organic substance (dextrine, gum arabic, cellulose—filter paper, starch, cane-sugar, etc.). The intensity of the coloration is proportional to the amount of silver present. The colour is sensitive enough to show the presence of silver in 50 c.c. of a solution containing one part of silver in 25,000,000 parts of solution; and it is possible to estimate 0·000002 grm. of silver in 50 c.c. of solution, *i.e.* 0·00004 grm. of silver per litre.[3]

Standard Solution.—Pipette 5 c.c. of the silver solution[4] into a 150-c.c. beaker. Dilute the solution to 50 c.c. Add a few drops of a concentrated solution of cane-sugar. Immerse the beaker in a bath of boiling water for 2 minutes; add 5 drops of an N-solution of sodium hydroxide, and heat the mixture for 20–30 seconds after the colour has appeared.[5] Cool the solution and transfer it to a burette.

Test Solution.—The silver solution under investigation is appropriately diluted and treated as described for the standard solution.[6] 50 c.c. of the solution are transferred to a Nessler's glass. The tint of this solution should be nearly the same as the tint of the standard solution. If not, either the standard or the test solution must be diluted, and the operations (development of colour) repeated.

The Comparison.—The standard solution is placed in a burette and run into a second Nessler's glass until the colour is of the same intensity in both vessels. The number of c.c. of the standard solution required to produce the same intensity of colour as that of the 50 c.c. of the test solution furnishes the necessary data for the calculation of the amount of silver in the test solution (pages 200 and 204).

Whitby says that ammonia should be absent, but minute traces of copper, zinc, mercury, bismuth, cadmium, and lead, in quantities insufficient to give an appreciable precipitate with sodium hydroxide, do not interfere with the result.

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[1] A. W. Clasen, *Journ. prakt. Chem.* (1), 97. 217, 1866. For reduction with hydroxylamine, A. Lainer, *Monats. Chem.*, 9. 533, 1888; with aluminium, N. Tarugi, *Gaz. Chim. Ital.*, 33. ii. 223, 1904; with cobalt, C. Goldschmidt, *Zeit. anal. Chem.*, 45. 87, 1906.

[2] See page 326; G. S. Whitby, *Ber. Internat. Congress App. Chem.*, 7. 12, 1910.

[3] F. Jackson, *Journ. Amer. Chem. Soc.*, 25. 992, 1903; W. Böttger, *Zeit. angew. Chem.*, 25. 1992, 1912.

[4] Silver Nitrate Solution.—The standard silver nitrate solution should contain the equivalent of about 0·00001 grm. of silver per c.c. The standard solution should be approximately the same strength as the test solution, and it should be prepared the same day the determination is made; otherwise its tint deepens if it be allowed to stand for any length of time.

[5] Do not heat more than about 2 minutes.

[6] If no coloration appears after the solution has been heated 2 minutes, it can be assumed that silver is absent.

§ 338. The Determination of Iodine.

Iodine, to the extent of 0·01–0·2 per cent., is not uncommonly present in mineral phosphates. It can be detected by digesting the finely powdered phosphate with concentrated sulphuric acid in a flask so arranged that a current of air is aspirated through the flask into a solution of carbon disulphide or chloroform. The pink or violet colour of the solution shows the presence of iodine. The iodine is of no known technical importance in the silicate industries. Hence, the subject can be dismissed very quickly.

Thiercelin[1] determines iodine in phosphates, etc., by digesting a large quantity of the substance, say 100 grms., with a mixture of equal parts of sulphuric acid and water in a 500-c.c. flask or retort arranged so as to conduct the vapours into potash lye contained in a suitable absorption tube, say, fig. 194. The mixture in the flask is boiled (about 30 minutes) until all the vapours of iodine have been driven into the absorption tubes. The solution of iodine in the potash is treated with an excess of sulphurous acid to convert the iodates, etc., into iodides: $SO_2 + 4KOH + I_2 = 2KI + K_2SO_4 + 2H_2O$.

The iodine absorbed by the lye can be determined as silver iodide by adding an excess of silver nitrate to the solution neutralised with nitric acid, and then adding an excess of nitric acid, in which silver iodide is almost insoluble.[2] The precipitated silver iodide is treated as if it were silver chloride (page 652); but silver iodide is not so readily reduced as the chloride, and it may even be safely ignited with the filter paper. The weight of silver iodide multiplied by 0·5405 gives the corresponding amount of iodine.

Sometimes iodine is determined as cuprous iodide[3] by adding a solution of ammonium cuprous chloride[4] to the solution of the iodide acidified with hydrochloric acid, and containing a sufficient excess of ammonium chloride to prevent the precipitation of cuprous chloride by the aqueous solution. The precipitated cuprous iodide is collected on a tared filter paper, or, better, in a Gooch's crucible, dried, and weighed as CuI. This method, however, offers no particular advantage over the silver iodide process.

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[1] M. Thiercelin, *Bull. Soc. Chim.* (2), **22.** 435, 1874.

[2] If the solution be first acidified with nitric acid, there is a risk of liberating iodine. If the solution be coloured with iodine, it is best to add a little sulphurous acid to decolorise the solution

[3] F. Mohr, *Zeit. anal. Chem.*, **12.** 366, 1873; H. Zenger, *Archiv Pharm.* (3), **3.** 137, 1873; J. Krutwig, *Ber.*, **17.** 341, 1884; E. Fleischer, *A System of Volumetric Analysis*, London, 97, 1877.

[4] Copper turnings are digested in a solution of cupric chloride and ammonium chloride acidified with hydrochloric acid. Sufficient ammonium chloride must be present to prevent the reagent giving a precipitate with water.

CHAPTER XLIV.

THE RATIONAL ANALYSIS OF CLAYS.[1]

§ 339. Clays.

THIS chapter is "brought forward" from the second volume of this work in order that the analytical processes may be confined in one volume. Hence, a few explanatory words may be desirable. *Kaolin* is a general word applied to *china clay rock*, and to *china clay* obtained by the washing of china clay rock. The term *clay* not only covers all the different varieties of clay, but also a substance approximating $Al_2O_3.2SiO_2.2H_2O$ in composition. The last-named formula is supposed to represent a constituent common to all clays, and which has hence been termed "clay base," "clay substance," "clay proper," "clay matter," "ideal clay," etc. The word *kaolinite* is applied to a crystalline mineral with the empirical formula $Al_2O_3.2SiO_2.2H_2O$. We are almost sure that an amorphous or non-crystalline substance approximating the same composition exists in most, probably in all clays. This is here called *clayite*; the new term is required because it possesses several properties different from kaolinite. If it were not for the dread of multiplying terms, a word would be coined to include both clayite and kaolinite. I use the term *argillaceous matter* for that heterogeneous mixture which is removed from a clay by the treatment employed in the method of "rational analysis." It includes clayite, kaolinite, and other minerals.[2]

Clays are produced by the weathering and disintegration of various kinds of rocks which occur on or near the surface of the earth. If the clay occurs where it has been formed, it is called a *primary or residual clay*; and if the clay has been carried elsewhere it is called a *transported or secondary clay*. The transported clays are the washings and sweepings of the hills, which Nature has accumulated as her rubbish-heaps in convenient places. Kaolinite or clayite and quartz are common to nearly all clays, while felspar and mica are so common in clays that these four constituents can reasonably be regarded as the *primary constituents* of clays. The list of *secondary constituents*, which usually occur in relatively small quantities, is very extensive. In the first place, we find fragments of various kinds of rock—granite, trachyte, rhyolite, syenite, etc.; and in the second place, fragments of numerous minerals have been reported in clays :—

Anatase, andalusite, apatite, augite, bronzite, calcite, chlorite, corundum, cyanite, diaspore, dolomite, dumortierite, enstatite, epidote, fluorspar, garnet, gilbertite, glaucophane, gypsum, hematite, hornblende, hydrated alumino-silicates related to clayite, hypersthene, ilmenite, leucoxene, lignite, limonite, magnesite, magnetite, nepheline, nontronite, olivene, prehnite, pyrites, rutile, scapolite, selenite, serpentine, siderite, sillimanite, spinel, staurolite, titanite (sphene), topaz, tourmaline, vivianite, zeolite, zircon, zoisite.

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[1] Much of the original matter in this chapter is the result of experiments made on the *rationale* of the method of rational analysis during the investigation of the composition of dusts for Sir Henry Cunynghame, Chairman of the *Committee appointed to Inquire into the Causes and Remedies for Coal Dust Explosions in Coal Mines.* The reader must thank the Chairman for permission to use such experiments as I thought fit for this chapter. Most were done by my assistants, Messrs A. D. Holdcroft and C. Edwards, during 1911.

[2] J. W. Mellor, *Trans. Eng. Cer. Soc.*, 8. 23, 1908; *Pot. Gaz.*, 34. 927, 1909.

The secondary constituents are usually present in small quantities, and in a more or less advanced state of decomposition. The *rational analysis* is an attempt to express the composition of a clay in terms of the primary constituent minerals.

§ 340. The Separation of Minerals by Treatment with Chemical Reagents.

Clay is a heterogeneous mixture of several different minerals. The chemical methods for estimating the minerals in clays, etc., are based on differences in the rates at which the various minerals are attacked by different reagents. The separation of the constituents of a clay which are soluble in water (page 630) is a comparatively simple example, whereas the digestion of clay with hydrofluoric acid is more complicated. Quartz, felspar, leucite, and minerals rich in silica are in general quickly decomposed by treatment with hydrofluoric acid under conditions where sillimanite, staurolite, topaz, tourmaline, zircon, and the titanium minerals are but little attacked; while mica, hornblende, and sphene are partially decomposed.[1] Unfortunately, the differences in the rates of attack of the more important minerals in clays by known reagents are not usually great enough to allow a perfect separation. Before one mineral is completely decomposed, others will have succumbed to the attack. Hence, the products of decomposition of the one mineral will be more or less contaminated with products derived from the partial decomposition of other minerals. Hydrochloric acid, for example, is frequently employed to remove iron oxides, and calcium, magnesium, and iron carbonates, from clays. But if the clay contains olivene, serpentine, chlorite, nepheline, epidote, leucite, and zeolites, the acid may do too much work, for these minerals are more or less decomposed by the same treatment. Similar remarks apply, *mutatis mutandis*, to the action of sulphuric acid. Compare with page 525.

The analysis of clays, etc., by digesting the powdered sample in sulphuric acid, followed by solutions of caustic alkalies, etc., was common enough at the end of the eighteenth and at the beginning of the nineteenth centuries, as is evidenced by the analyses of Bergmann, Hochmeimer, Kirwan, Klaproth, Lampadius, Schönbauer, Vauquelin, Westrumb, etc.[2] In 1835, Forchhammer[3] showed that, when certain clays are digested in sulphuric acid, the ultimate composition of the soluble portion corresponds very nearly with the formula $Al_2O_3 . 2SiO_2 . 2H_2O$; while the residual insoluble portion is mainly felspar and quartz. Hence, Forchhammer attempted to determine the mineralogical composition of certain clays by successive treatment with different reagents. After leaching out the constituents soluble in hydrochloric acid, he extracted the residue alternately with hot sulphuric acid and an aqueous solution of sodium carbonate. This treatment was supposed to remove the argillaceous matter. We shall, however, soon see that a variety of other minerals—mica, felspar, fluorspar, etc.—are more or less attacked by this treatment. Forchhammer's process has been more or less modified by Brongniart and Malaguti, Seger,[1] etc., and extensively employed—principally in Germany—with Brongniart's designation, *l'analyse rationelle.* The so-called rational analysis is a first approximation or attempt to represent the mineralogical composition of a clay in terms of the three important minerals—kaolinite, felspar, and quartz—and hence it can also be called a "mineralogical analysis," *vide* page 524. The essential features of the process are :—

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[1] F. Fouqué, *Compt. Rend.*, **75**. 1090, 1872; **79**. 869, 1874; F. Fouqué and M. Levy, *Minéralogie Micrographique*, Paris, 116, 1879; J. B. Mackintosh, *School Mines Quart.*, **7**. 384, 1886; *Journ. Amer. Chem. Soc.*, **8**. 210, 1886; *Chem. News*, **54**. 102, 1886. Mackintosh believes that, the denser the mineral, the less is it attacked by the acid; and that the rate of attack by hydrofluoric acid does not depend upon the proportion of silica, but rather on the nature of the bases. K. Obbeke, *Neues Jahrb. Min.*, **1**. 455, 1881; J. Hazard, *Zeit. anal. Chem.*, **23**. 158, 1884; *Chem. News*, **50**. 33, 1884.

[2] T. Bergmann, *Opuscula Physica et Chemica*, Holmiæ, **2**. 399, 1780; C. F. A. Hochmeimer, *Mineralogische Chemie*, Leipzig, 1792; R. Kirwan, *Physisch-chemische Schriften*, Berlin, 1783; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, 1795; W. A. Lampadius, *Handbuch zur chemischen Analyse der Mineralkörper*, Freiberg, 1801; J. A. Schönbauer, *Neue analytische Methode die Mineralien und ihre Bestandtheile Richtig zu Bestimmen*, Wien, 1805; L. N. Vauquelin, "Anleitung zur chemischen Analyse der Fossilen," *Scherer's Journ.*, **3**. 410, 1799; J. F. Westrumb, *Kleine physisch-chemische Abhandlungen*, Leipzig, 1785.

[3] G. Forchhammer, *Pogg. Ann.*, **35**. 331, 1835; *Ann. Mines* (3), **7**. 517, 1835.

Remove the argillaceous matter by digestion with hot concentrated sulphuric acid, and wash the residue alternately with alkaline lye and hydrochloric acid. The difference between the weight of the dried residue and the original sample represents argillaceous matter. The residual felspathic and quartz detritus is treated with hydrofluoric acid and the alumina determined. The corresponding amount of felspar is computed, and the quartz is determined by difference. One *modus operandi* is as follows :—

§ 341. The Rational or Mineralogical Analysis of Clays.

Preliminary Treatment.—If the clay contains soluble salts, they are removed by the process indicated on page 630; if it contains colloidal silica, this can be removed as indicated on page 668; and if it contains carbonates—calcium, magnesium, iron—or free iron oxide, these should be removed by digesting, say, 5 grms. with dilute hydrochloric acid (page 525) before treatment with sulphuric acid. The hydrochloric acid also removes colloidal aluminium and iron hydroxides, and it attacks some of the argillaceous matters, as well as apatite, hæmatite (powdered), magnetite, leucite, sodalite, nepheline, olivine, wollastonite, and most of the zeolites; while scapolite, plagioclase, serpentine, chlorite, and the more compact iron oxides are but slowly attacked. Hence, Weinschenk[2] recommends chloric acid, in place of hydrochloric acid, to avoid breaking up silicates when the carbonates are decomposed. The washed residue is dried and weighed. The loss in weight represents the matters soluble in the acid. The carbon dioxide, if desired, can be determined by weight as described later, and the lime, magnesium, and iron determined in the acid solution if necessary. If the carbon dioxide be determined by weight (page 553), the washed residue, or a new sample, can be treated with sulphuric acid, etc., as described below, and an allowance made when the clay substance is determined.

In illustration, Altofts' shale furnished 4·42 per cent. of carbon (page 546) and 2·44 per cent. of carbon dioxide (page 553). The solution of the shale in hydrochloric acid contained much iron, and very little lime or magnesia. Hence it was inferred that the shale contained ferrous carbonate. One part by weight of carbon dioxide corresponds with 2·633 of ferrous carbonate, and accordingly the shale contained the equivalent of $2{\cdot}44 \times 2{\cdot}633 = 6{\cdot}42$ per cent. of ferrous carbonate.

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[1] A. Brongniart and J. Malaguti, *Arch. Mus. Hist. Nat.*, **2.** 219, 1841; J. Aron, *Notizblatt*, **10.** 226, 1874; M. Finkner, *ib.*, **3.** 119, 1867; C. Bischof, *ib.*, **11.** 120, 1875; H. A. Seger, *ib.*, **12.** 245, 1876; *Tonind. Ztg.*, **1.** 272, 1877.

[2] B. Weinschenk, *Die gesteinbildenden Mineralien*, Freiburg, 11, 1907; New York, 150, 1912. For the action of organic acids on minerals, see page 525.

Removal of Argillaceous Matters.—The residue from the preceding operation; or, if carbonate be absent, about 5 grms. of the clay, dried at 110°, are placed in a litre basin (porcelain or platinum). Add 100 c.c. of water, and triturate the mixture with a rubber-tipped glass rod or rubber pestle, so that the clay is thoroughly disintegrated.[1] This operation diminishes the risk of clay escaping the action of the acid when clots of clay are present. Add 100 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water to the clay "slip." Cover the basin with a clock-glass. If the clay is dark-coloured, add a few drops of concentrated nitric acid, so as to destroy the organic matter.[2] Warm the mixture over an Ostwald's heater (page 94), with frequent stirring, until the water is all evaporated and the acid begins to fume vigorously. The temperature should be such that this occupies between 45 and 60 minutes. The dish is allowed to cool for about half an hour, and the dish is then nearly filled with water[3] and the whole thoroughly mixed. Wash the rod and cover-glass. Let the dish stand undisturbed for about four hours to permit the unattacked particles of the clay to settle. Decant the contents of the dish into a large 2-litre beaker. Take care that no solid particles are transferred from the dish.[4] Add 300 c.c. of Lunge's solution,[5] and heat the mixture, with frequent stirring, until it begins to boil. Wash the rod and cover-glass. Let the mixture cool for about a couple of hours. The fluid should be clear. If the sediment does not settle, so that flocculent masses remain in suspension,[6] it is probable that the clay is but imperfectly decomposed.[7] Decant off the alkaline lye, stir up the residue with about 500 c.c. of concentrated hydrochloric acid, and boil the mixture for about five minutes; this dissolves the iron hydroxide, etc. Stir up with water. Let all stand for about five hours. Decant off the acid.[1] Repeat the treatment with about 150 c.c.of Lunge's solution, followed by digestion with 200 c.c. of hydrochloric acid. Stir up the mass with about 200 c.c. of water and wash the residue with dilute hydrochloric acid (1 volume of acid, 2 volumes of water) into a close-felted filter paper,[2] and wash twice with the dilute acid, and three times with water. Ignite the filter papers with their contents in a weighed platinum crucible. The ignited residue is generally styled "felspar and quartz," and treated as described below. The difference between the weight of clay subjected to the sulphuric acid treatment and the weight of the "felspar and quartz" represents "argillaceous matter"—also called "clay substance." In illustration of the weighings, and method of calculation, the rational analysis of Altofts shale[3] may be cited :

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[1] The addition of a drop or two of aqueous ammonia or soda lye greatly facilitates the disintegration of the mass. Boiling the mixture for about 10 minutes will also facilitate the disintegration of the clay. Any water lost by evaporation should be restored. The clay must not be powdered in an agate mortar for this operation, as is done with the ultimate analysis.

[2] If the clay contains organic matter—lignite, rootlets, etc.—A. Sabeck (*Chem. Ind.*, 25. 90, 1902) recommends oxidation with about 15 c.c. of nitric acid along with the sulphuric acid after the clay has been digesting with the sulphuric acid for a couple of hours. If chloric acid be used for decomposing the carbonates, much of the organic matter will be removed at the same time. Note, organic matter is included with "argillaceous matter" by this method of treatment. The error, if neglected, is serious with some clays—*e.g.* black ball clays.

[3] Care is necessary in adding water to concentrated sulphuric acid. Some prefer to lift the cover of the dish a little, and spurt water from the wash-bottle on the under side of the clock-glass.

[4] In pouring off the bulk of the fluid (down a glass rod in the usual way) the sediment is disturbed. It is best to decant all but about 100 c.c. of the fluid. Let this stand about 15 minutes to settle, and again decant. This enables more liquid to be poured off with less risk of losing the solid insoluble residue.

[5] LUNGE'S SOLUTION.—Dissolve 100 grms. of crystallised sodium carbonate and 10 grms. of sodium hydroxide in water, and make the solution up to a litre. Remember that this solution will dissolve silica, etc., from the glass of the bottle in which it is kept. A five or six per cent. solution of caustic soda is frequently used in place of Lunge's solution. Different workers also prescribe different strengths of the solution of caustic soda, as indicated below. Lunge's solution is fairly well known, and there is at present no adequate reason for recommending a change.

[6] Flecks of silicic acid, organic matter, and iron hydroxide will probably be present.

[7] J. A. Körner (*Beitrag zur Kenntniss der Elsässer Thone*, Strassburg, 1900) removes the soluble silica left after the action of the sulphuric acid as follows:—Wash the residue from the sulphuric acid treatment with dilute hydrochloric acid (1 : 3) and incinerate the residue to burn off the filter paper. Digest the mass on a water bath for five minutes with 0·5 per cent. hydrofluoric acid; filter, and wash with dilute hydrochloric acid; ignite; and weigh as "quartz and felspar." Hydrofluoric acid of this strength is said not to attack the quartz appreciably.

Crucible and residue	35·3236 grms.
Crucible empty	33·2950 ,,
Quartz and felspar	2·0286 ,,
Clay originally taken	5·0000 grms.
Argillaceous matter[4] (difference)	2·9714 ,,

Hence, 59·43 per cent. of matter has been removed by the treatment with sulphuric acid, etc., and 40·57 per cent. remains as a residue. A preceding operation showed that of the 59·43 per cent. of matter dissolved by the sulphuric acid, there is :

Argillaceous matter	48·59 per cent.
Ferrous carbonate (siderite)	6·42 ,,
Carbonaceous matter	4·42 ,,

Estimation of the Felspathic and Quartz Detritus.—The residue in the crucible is mixed with about 5 c.c. of water, about 4 drops of sulphuric acid, and 15 c.c. of hydrofluoric acid.[5] The crucible is then placed on a sand-bath or over a small flame and heated until its contents are nearly dry. Repeat the operation by the addition of more hydrofluoric acid. Let the mass cool, digest with water, and add ammonium chloride and ammonia as indicated on page 182 for the precipitation of iron and aluminium hydroxides. Filter, wash with hot water, ignite, and weigh. Call the mixture of alumina, iron oxide, etc., "alumina." Thus, with the clay indicated above:

Crucible and contents	33·3477
Crucible empty	33·2986
"Alumina" precipitate	0·0491

Since one gram of alumina corresponds with 5·48 grms. of potash felspar, hence multiply the weight of the precipitate by 5·48 to get its equivalent in potash felspar.[1] We thus obtain 5·48 × 0·0491 = 0·2691 grm. of felspar per 5 grms. of clay—that is, 5·38 per cent. of felspar.[2] The difference

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[1] If flecks of clay be present, the sulphuric acid has not done its work. The residue is usually more or less gritty, although flecks of organic matter may be present.

[2] Note that in the filtration very fine particles of undecomposed felspar and quartz have a tendency to pass through the paper, and thus swell the proportion of argillaceous matter, at the expense of the residue.

[3] I have purposely selected an awkward clay, because it enables me to emphasise the strength and weakness of the process of rational analysis.

[4] The filter papers used were almost ashless.

[5] M. Lindhorst, *Tonind. Ztg.*, 2. 435, 1878; K. Daniel, *Zeit. anorg. Chem.*, 38. 257, 1904. H. Rose's method (*Pogg. Ann.*, 108. 20, 1859) for driving off the silica by thoroughly mixing the sample with ammonium fluoride in an agate mortar and moistening with sulphuric acid may be employed. Let the mixture stand in a warm place for a few hours, heat until the silicon fluoride has been driven off, and repeat the treatment if any of the mixture has escaped decomposition. Fusion with sodium carbonate (page 167), as first recommended by Seger, is not so convenient.

Felspar and quartz residue	40·57	per cent.
Felspar calculated	5·35	,,
Quartz *débris*	35·22	,,

Neglecting the second decimal, the rational analysis thus reads:

Carbonaceous matter	4·4	per cent.
Ferrous carbonate (siderite)	6·4	,,
Argillaceous matter	48·6	,,
Felspathic detritus	5·4	,,
Quartz *débris*	35·2	,,

Errors.—Apart from the difficulties which arise from our ignorance of the nature of the constituent minerals, and the fact that the acid and alkaline solutions do more work than accords with the hypothesis on which the process is based, the chief errors of manipulation are: (1) Incomplete decomposition of the kaolinite or clayite; (2) Imperfect removal of the products of the decomposition. These two errors make the felspathic detritus too high, and the argillaceous matter too low. (3) Loss of a portion of the felspathic and quartz detritus either during the decantation[3] or by passage through the pores of the filter paper. This error makes the argillaceous matter too high, and the felspathic detritus too low.

The whole operation occupies about two days. If a start be made in the morning, the first alkali and hydrochloric acid decantations can generally be done the first day. Of course, other work can be done while the sediments are settling. Thus, two analyses can be conducted side by side in two days. In order to get comparable or consistent results, it is highly important to follow the directions—concentration of reagents, time of heating, etc.—somewhat closely. The reason for this will now be discussed.

§ 342. The Effect of the Sulphuric Acid Treatment on some of the Minerals in Clays.

Sulphuric acid decomposes the hydrated alumino-silicates and zeolites forming aluminium sulphate, silicic acids, etc. The soda treatment removes the latter, hydrochloric acid the former. At the same time, the soda attacks[4] the felspar somewhat rapidly, while the accessory minerals hornblende, augite, and biotite are attacked rather more slowly. Andalusite, epidote, prehnite, and muscovite are but slightly attacked by the same reagent. It is therefore interesting to get some idea of the effect of the treatment with sulphuric acid, caustic soda, and hydrochloric acid on the minerals usually found in clays. The samples were treated exactly as if they were being analysed by the "rational" process just described.

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[1] Attempts to remove felspar from the first residue by digesting the mixture at 200° with alkaline phosphates and with microcosmic salt have not been successful, because the finely divided quartz is seriously attacked at the same time as the felspar—A. Müller, *Journ. prakt. Chem.* (1), **95**. 43, 1865; (1), **98**. 14, 1865; *Zeit. anal. Chem.*, **5**. 431, 1866; E. Laufer, *ib.*, **17**. 368, 1878; *Ber.*, **11**. 60, 935, 1878; E. Wunderlich, *ib.*, **14**. 368, 2811, 1881; J. Hirschwald, *Journ. prakt. Chem.* (2), **41**. 360, 1880; E. A. Wülfing, *Neues Jahrb. Min. B. B.*, **7**. 174, 1891; K. Haushofer, *Sitzber. Acad. Wiss. München*, 8, 1889. See page 520.

[2] Some consider that a more exact determination of felspar can be obtained by determining the alkalies and not the alumina by the method of page 226.

[3] To avoid this error, some prefer to filter the decanted fluid, and wash the residue with the acid and alkaline lye. E. Greiner, *Sprech.*, **42**. 399, 413, 1909.

[4] J. Lemberg, *Zeit. deut. geol. Ges.*, **35**. 560, 1883.

1. *Felspar.*—The felspar in clays is attacked by the sulphuric acid treatment, and finely divided felspar more vigorously than the coarse-grained mineral. In illustration, clear[1] crystals of albite (soda felspar) from Maderanertæ (Switzerland), and clear crystals of orthoclase (potash felspar) from Altschgletscher (Switzerland), were powdered, and treated as if they were samples undergoing "rational analysis" by the method described above. The results were:

	Coarse.	Fine.	
Average diameter of grain	0·082	0·032	mm.
Albite dissolved	1·76	14·69	per cent.
Orthoclase dissolved	0·86	13·01	,,

The term "coarse" here refers to powder which passed through a 120's lawn and remained on a 200's lawn, while "fine" refers to that which passed through the 200's lawn.[2] In further illustration of the effect of size of grain another series of determinations with a clear glassy sanidine from Wehr (Eifel) furnished:

Average diameter of grain . .	0·165	0·082	0·032	mm.
Sanidine dissolved . . .	0·34	0·64	15·64	per cent.

These results are plotted in fig. 205, which brings out the fact that, although the effect of the treatment on coarse-grained felspar is negligible, the effect on the small grains is vigorous. Sabeck says that if the clay contains no more than 10 per cent. of felspar, "the total error introduced by the decomposition of felspar by the sulphuric acid treatment does not exceed 0·2 per cent." under the conditions of his experiments, which were not very different from those mentioned above. Sabeck's results agree with those obtained by Seger (2·24 per cent. dissolved) and Jackson (2·24). With Langenbeck, 17·3 per cent. dissolved.[3] It might be thought that fig. 205 makes it questionable if Sabeck's argument is sound, because many of the felspathic grains in felspathic clays may be finer than can be obtained by artificial grinding, although it is probable that, if felspar so finely divided were deposited with the original clay, it would have weathered or changed comparatively quickly.

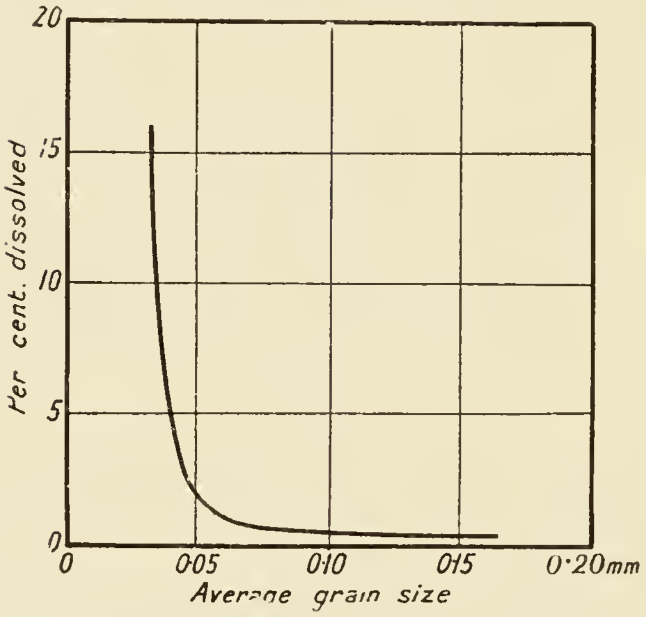

FIG. 205.—Effect of grain size on the solubility of potash felspar.

There is some uncertainty as to the composition of the particular felspar or felspars in a given clay. It is not easy to get felspar free from symptoms of weathering, for even the so-called clear crystals are usually affected. Much more then is it probable that the felspathic grains in clays will be more or less weathered. Weathered felspar dissolves rapidly in sulphuric acid. Consequently, it is not surprising to find results so divergent as 2·5 (Seger) and 17·3 (Langenbeck), even when the conditions of the experiment and the degree of fineness of the felspar undergoing treatment are the same.

The attack is largely determined by the concentration of the different reagents, as well as the duration and temperature of the digestion with sulphuric acid, etc. It is therefore necessary to arrange conditions such that the felspar is affected as little as possible. It is a disadvantage to have the sulphuric acid too dilute, for it will then change considerably in volume during the digestion, and particles of the clay may be left on the sides of the dish, as water evaporates, and consequently remain unattacked.[1] Sufficient acid must also be present to ensure the decomposition of all the argillaceous matters.

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[1] These samples were selected because they were clear and free from any visible signs of weathering.

[2] J. W. Mellor, *Trans. Eng. Cer. Soc.*, **9.** 94, 1909. See page 126.

[3] H. Rose, *Scheerer's Journ.*, **8.** 233, 1803; H. A. Seger, *Notizblatt*, **12.** 245, 1876; *Gesammelte Schriften*, Berlin, 42, 1896; Easton, Pa., **1.** 53, 1902; K. Langenbeck, *The Chemistry of Pottery*, Easton, Pa., 9, 1895; W. Jackson and E. M. Rich, *Journ. Soc. Chem. Ind.*, **19.** 1087, 1900; A. Sabeck, *Chem. Ind.*, **25.** 90, 1902.

2. *Mica, Nepheline, and Hornblende.*—If mica be present in the clay, as it usually is, it will be more or less attacked by the treatment. Some varieties of mica—phlogopite, for instance—will be almost completely decomposed along with the kaolinite. As in the case of felspar, the experimental evidence shows that the attack is dependent upon the type of mica present in the clay, the concentration of the reagents, the time of heating, and the state of subdivision of the mica. Here are some results with selected samples of mica treated by the same process as that employed for the felspars :—

Effect of Rational Analysis on Mica (per cent. dissolved).

Size of grain (average diameter, mm.).	Muscovite. Clérmont Ferrant (Auvergne).	Lepidolite. Rozna (Mähren).	Biotite. Miask (Ural).	Phlogopite. Ontario (Canada).
Coarse—0·087 . . .	54·94	67·94	71·07	88·00
Fine—0·040 . . .	55·56	70·02[2]	92·50[3]	93·93

This shows that mica is rapidly attacked by the method of rational analysis, and part will be found in the soluble portion and part with the insoluble residue left after the sulphuric acid treatment.

It might be added that similar experiments with a sample of hornblende from Moravicza (Austria), and a sample of nepheline from Vesuvius (Italy), gave :

	Coarse.	Fine.
Hornblende dissolved	1·79	15·09 per cent.
Nepheline dissolved	98·63	99·62 ,,

3. *Quartz.*—The acids appear to have no appreciable effect on the quartz, but quartz is affected by the caustic soda treatment. Brongniart and Malaguti substituted a solution of caustic soda for Forchhammer's sodium carbonate. The action of caustic soda on quartz has been studied in some detail. Michaelis,[4] in opposition to earlier workers, maintained that quartz is not appreciably affected by a 10 or 15 per cent. solution of caustic soda when digested on a water bath with this reagent. This observation also contradicts the later work

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[1] C. Bischof (1884) and H. Hecht (1895) recommended an acid 1 : 6 ; H. A Seger (1875), C. Bischof (1904), G. Lunge (1908), and A. Sabeck (1903), 1 : 3 ; H. A. Seger (1893), A. Leopold (1905), and E. Berdel (1903), 1 : 2 ; and B. Zschokke (1902), 1 : 1.

[2] Another sample gave respectively 46·3 and 48·2 per cent.

[3] Another sample gave 60·97 and 89·2 per cent. respectively.

[4] W. Michaelis, *Chem. Ztg.*, **19**. 1422, 2002, 2296, 1895 ; C. Rammelsberg, *Pogg. Ann.*, **112**. 182, 1861 ; J. N. Fuchs, *ib.*, **31**. 577, 1834 ; G. Jenzsch, *ib.*, **126**. 497, 1865 ; T. Scheerer, *Berg. Hütt. Ztg.*, **14**. 107, 1858 ; O. Maschke, *Zeit. deut. Geol. Ges.*, **7**. 438, 1855 ; A. Müller, *Journ. prakt. Chem.* (1), **98**. 14, 1866 ; C. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1**. 207, 1873 ; **2**. 338, 1877 ; H. Rose, *Handbuch der analytischen Chemie*, Leipzig, **1**. 751, 1871.

of Lemberg and Rinne,[1] who have shown that finely divided quartz is readily dissolved by this treatment. We must therefore assume that Michaelis was dealing with comparatively coarse grains of quartz, which are fairly resistant. Lunge and Millberg have shown that the solubility of quartz depends upon the fineness of the particles, the concentration of the reagent, and the time of heating—*e.g.* a 15 per cent.-solution of caustic potash dissolves from 1·0 to 1·5 per cent. of finely divided quartz in an hour's digestion, and 1·8 to 2·0 per cent. after two hours' digestion under conditions where a 15 per cent. solution of sodium carbonate dissolved only mere traces of the quartz. The attack is nearly ten times more vigorous when the quartz is in an extremely fine state of division. The experiments indicated above were repeated on a sample of clear rock crystal, and on a sample of flint from Dieppe (France). The results were :

	Coarse.	Fine.
Rock crystal	0·96	6·40
Flint	2·52	12·10

The experimental evidence thus shows that quartz is appreciably attacked when the clay is digested with caustic soda in order to remove the so-called colloidal silica, or the silicic acids formed during the action of sulphuric acid. Of course, if the caustic soda be dilute enough, and is only in contact with the quartz a short time, the action may be reduced to a negligible minimum ;[2] but

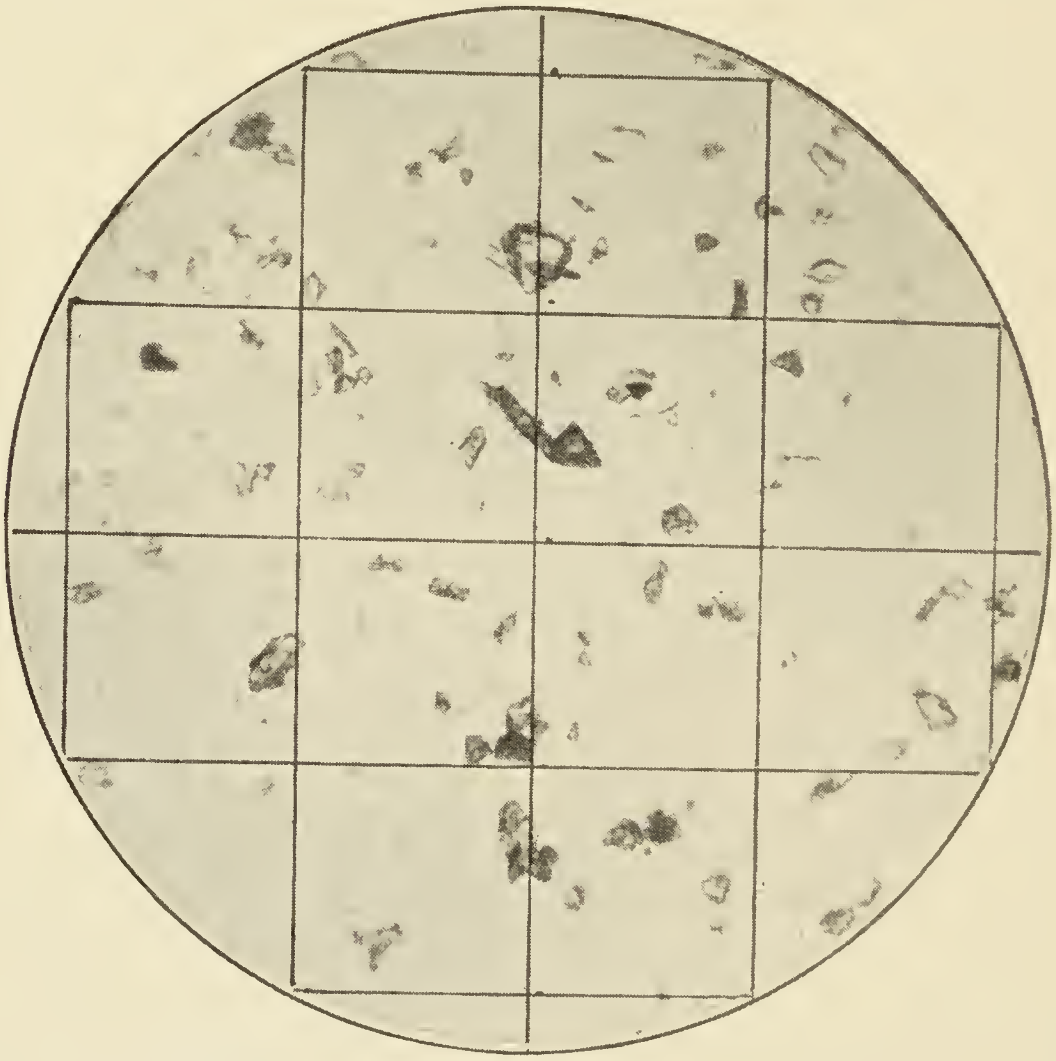

FIG. 206.—Residue obtained during the rational analysis of shale. (The lines are $\frac{1}{100}$ mm. apart when not magnified.)

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[1] J. Lemberg, *Zeit. deut. geol. Ges.*, **35**. 560, 1883 ; F. Rinne, *Zentr. Min.*, 334, 1904 ; E. Kaiser, *Verh. nat. Ver. preuss. Rheinlande*, **54**. 93, 1897 ; *Zeit. Kryst.*, **33**. 200, 1900 ; A. Sabeck (*l.c.*) ; B. Zschokke (*l.c.*) ; G. Lunge and M. Schochor-Tscherny, *Zeit. angew. Chem.*, **7**. 485, 1894 ; **8**. 593, 689, 1895 ; G. Lunge and C. Millberg, *ib.*, **10**. 393, 425, 1897 ; P. Kreiling, *G. Lunge's Methods of Chemical Analysis*, London, **1**. ii., 585, 1908.

[2] A. Sabeck, (*l.c.*) recommends a 2 per cent. solution of caustic soda ; E. Berdel (*l.c.*), a 6 to 7 per cent. solution.

the minimum may be quite appreciable if the quartz in the clay be in a very fine state of subdivision. For this reason, Kreiling, and Lunge and Millberg, returned to the use of sodium carbonate as employed by Forchhammer, in order that the quartz and felspar may be attacked as little as possible when the products of the action of the sulphuric acid are being removed.

Fig. 206 represents a microphotograph of the residue obtained during the rational analysis of a sample of shale, and the sharp angularity of the grains shows that the attack, during the removal of the "argillaceous matter," was not very marked with the larger grains. The lines in the diagram are $\frac{1}{100}$th millimetre apart when not magnified.

§ 343. The Composition of the "Argillaceous Matter."

The term *Thonsubstanz* (clay substance) was applied by Senft[1] in 1867 to a hydrated aluminosilicate which is supposed to occur in all clays and to which they owe their plasticity. Senft's clay substance was, in 1840, Brongniart and Malaguti's *la véritable argile*; and other writers have expressed the same idea by the use of such terms as "ideal clay," "Kaolinthon," etc. (page 656). Aron and Seger applied the term to the finest fraction obtained in the elutriation of clays, and also to the constituents decomposed by the action of concentrated sulphuric acid, thus implying that the clay substance in clays can be isolated or removed by both these processes. Kaolinite and clayite usually occur in an extremely fine state of subdivision, and consequently accumulate in the finest fraction of the elutriation. But if, as is frequently the case, other finely divided constituents occur in the clay, they too will naturally collect in the fine fraction. These constituents may or may not behave like kaolinite when the clay is treated with sulphuric acid, etc. Hence the use of the one term "clay substance" for totally distinct concepts must lead to confusion and misunderstanding.[2]

Not only are kaolinite and clayite attacked by the treatment with sulphuric acid, etc., but the felspar, mica, and quartz, as well as pyrites, zeolites, fluorspar, hornblende, etc., present in smaller proportions are also attacked. It is therefore necessary to investigate the composition of the product of the reaction in question. The analyses of the argillaceous matter in six different Cornish china clays on the market, dried at 110°, furnished the following table:

Percentage Composition of the Argillaceous Matter of China Clays.

	Maxima.	Minima.	Mean of six.	Ideal clay, $Al_2O_3 . 2SiO_2 . 2H_2O$.
Silica (SiO_2)	46·37	45·14	45·6	45·5
Titanic oxide (TiO_2)	1·11	0·08	0·5	...
Alumina (Al_2O_3)	40·28	38·19	39·2	39·5
Ferric oxide (Fe_2O_3)	1·48	0·52	1·0	...
Magnesia (MgO)	1·28	0·10	0·2	...
Lime (CaO)	1·41	0·25	0·3	...
Potash (K_2O)	1·36	0·52	1·0	...
Soda (Na_2O)	0·80	0·11	0·4	...
Loss on ignition	14·12	11·03	12·5	14·0

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[1] F. Senft, *Die Steinschutt und Erdboden*, Berlin, 236, 1867.

[2] Elutriation is discussed in the second volume of this work, and I here employ the term "argillaceous matter" for that heterogeneous mixture removed by the sulphuric acid treatment.

These clays contained from 80 to 98 per cent. of "argillaceous matter." As a result of similar experiments on German clays, Seger[1] drew the obvious conclusion: *The main constituent of certain high-grade clays is dissolved by the sulphuric acid treatment, and it corresponds in composition with* $Al_2O_3.2SiO_2.2H_2O$. Of course, it is not fair to apply this generalisation to all the different types of clays, since with other less pure clays very great discrepancies occur—see table below for an example. In spite of this, many call the matter decomposed by the sulphuric acid "clay substance," implying that this is a universal and essential constituent of all clays; when the fact is *that clay substance derived from a wide range of different types of clay is very varied in composition.*[2]

Since the argillaceous matter includes the more important constituents of clay—rarely falling below 50 per cent. of the total constituents, and sometimes ranging up to 99 per cent.—it is almost as important to get an idea of its mineralogical composition as it is of the clay itself. It is also better to use the general term "argillaceous matter" in preference to "clay substance," because the latter leaves the impression that we connote a substance $Al_2O_3.2SiO_2.2H_2O$, represented by analyses resembling those in the above table.

A Second Approximation to the Rational Analysis.—If the ultimate composition of the clay, and of the fractions which resist and succumb to the sulphuric acid treatment, be determined, it is possible to compute numbers for the argillaceous and felspathic matters which are more promising than those given by the method of page 660. The data for Altofts shale are indicated in the following table:

Analyses of Altofts Shale.

	Ultimate analysis.			
	Total.	Residue.	Argillaceous matter.	
Silica	51·92	38·77	13·15	
Titanic oxide	0·87	0·04	0·83	
Alumina	20·08	0·88	19·20	
Ferric oxide	6·40	0·06	6·34	10·81
Magnesia	1·58	0·01	1·57	
Lime	0·57	0·01	0·56	
Potash	2·72	0·83	1·89	
Soda	0·86	0·41	0·45	
Loss on ignition	14·61	0·00	14·61	
Totals	99·61	41·01	58·63	

All but the silica and titanic oxide in the residue (column 3) is supposed to be derived from the felspathic minerals. In typical potash felspar, $K_2O.Al_2O_3.6SiO_2$, one part of alumina corresponds with 3·53 of silica; and in typical soda felspar, $Na_2O.Al_2O_3.6SiO_2$, one part of alumina corresponds with 3·53 parts of silica. Hence,

$$\text{Silica in felspar} = (0{\cdot}83 \times 3{\cdot}51) + (0{\cdot}41 \times 3{\cdot}53) = 4{\cdot}37 \text{ per cent.}$$

The difference between this silica and the total silica in the residue represents the quartz. Hence, 38·77 less 4·37 = 34·4. Assume that the other constituents in the residue all belong to the felspar. Add these together and we get 6·6. For the reasons indicated on page 658, we know that the argillaceous matter is contaminated with carbon and siderite. Hence, we must subtract 4·4 per cent. of carbon and 6·4 per cent. of siderite. This leaves 58·63 - 4·4 - 6·4 = 47·8 per cent. of argillaceous matter. This gives :

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[1] C. R. Fresenius, *Journ. prakt. Chem.* (1), 57. 65, 1852; H. A. Seger, *Notizblatt*, 12. 245, 286, 1876; C. Loeser, *Kritische Beachtung einiger Untersuchungsmethoden der Kaoline und Thone*, Halle a.S., 18, 1905; *Tonind. Ztg.*, 32. 1932, 1908.

[2] The identification of the aluminosilicates—clayite or kaolinite, halloysite, etc.—will be discussed in Volume II.

Carbon	4·4	per cent.
Ferrous carbonate	6·4	,,
Argillaceous matter	47·8	,,
Felspathic detritus	6·6	,,
Quartz	34·4	,,

which is very close to the result obtained experimentally on page 661.

Computation of the Amount of Mica in the Argillaceous Matter.—I have seen rational analyses of one clay from French and German laboratories reported in terms of clay substance, mica, and quartz in the former case ; and clay substance, felspar, and quartz in the latter. Some regularly assume that the argillaceous matter contains kaolinite or clayite and mica. Given the ultimate composition of the argillaceous matter, it is sometimes but not always possible to calculate the corresponding proportion of mica and kaolinite or clayite. An average mica is taken to be :

Silica	46·2	per cent.
Alumina	40·2	,,
Fluxes (Fe_2O_3, MgO, CaO, K_2O, Na_2O)	12·5 to 11·2	,,
Water	2·4	,,

Here, 11·2 to 12·5 of fluxes represent 100 parts of mica, or 1 of fluxes represents about 8·5 parts of mica. Given, therefore, a clay whose ultimate composition is that represented in the second column of the above table, and the ultimate composition of the residue left by the sulphuric acid treatment that represented in the third column, the mica can be calculated as follows :—

The difference between the ultimate composition of the residue and of the whole clay obviously represents the composition of the argillaceous matter. This is shown in the last column of the above table.[1] The iron belonging to the ferrous carbonate is here included with the fluxes, which by hypothesis are associated with the argillaceous matter as mica. Hence deduct (6·4 × 0·687 =) 4·4 of ferric oxide from the fluxes. This leaves (10·8 - 4·4 =)6·4 per cent. of fluxes. Multiply the total amount of the fluxes, 6·4, in the argillaceous matter by 8·5, as indicated above. The result :

$$\text{Mica in argillaceous matter} = 6{\cdot}4 \times 8{\cdot}5 = 54{\cdot}4 \text{ per cent.}$$

Subtract this number, 54·4, from 47·8, and we get an absurd result. This means that *the fundamental assumption that the alkalies, etc., in the argillaceous matter are wholly derived from mica is false.*

With some clays the results seem to be satisfactory, and the method was used extensively by Vogt[2] and by Lavezard in their studies on the clays of France. I have considered it better to give a failure rather than to select a clay with which the process is more or less satisfactory. There must always be a considerable amount of uncertainty owing to our ignorance of the particular type of mica in the given clay. One feature in the calculation is that it reveals how investigators, dissatisfied with Seger's method of rational analysis, are groping for further light on this subject. Virtually we have tried to rationally analyse the results of a rational analysis, and failed.

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[1] The microscopic examination of a clay will generally show the presence or absence of mica —usually the former.

[2] G. Vogt, *Bull. Soc. d'Encour. l'Ind. Nat.* (5), **2**. 633, 1897 ; *Contribution à l'Étude des Argiles et de la Céramique*, Paris, 193, 1906 ; E. Lavezard, *ib.*, 113, 1906 ; E. Berdel, *Sprech.*, **36**. 1483, 1903 ; K. Langenbeck, *The Chemistry of Pottery*, Easton, Pa., 9, 1895.

Leopold's Process of Rational Analysis.—This leads us to Leopold's method of conducting the rational analysis,[1] which has been used in a modified form by others. After digesting the clay with sulphuric acid and water in the usual manner, instead of treating the residue with soda, etc., Leopold dilutes the contents of the basin with water; cools; adds ammonia until the solution reacts alkaline; filters; washes with hot water; dissolves the precipitate in hydrochloric acid, and makes the mixture up to 250 c.c. with water. The alumina, iron oxide, and lime are determined in aliquot portions. Multiply the amounts of alumina by 6·336 to get the kaolinite; the iron oxide can be calculated to Fe_2O_3, or to nontronite, $Fe_2O_3 . 2SiO_2 . 2H_2O$; the lime may be computed as if it were gypsum, if the ultimate analysis shows this mineral is present in appreciable quantities; the alkalies in the filtrate from the alumina precipitate are calculated to muscovite; and the alkalies in the residue on the filter paper, after the removal of the ammonia precipitate, are calculated to felspar.

These methods are highly artificial, and the results are affected by an uncomfortable number of assumptions. The pseudonym "rational analysis" has misled many to believe that the results are as trustworthy as, or even more trustworthy than, those furnished by a regular ultimate analysis. Sometimes, in fact, the rational analysis appears to be highly irrational. The truth is that in some cases the rational analysis is accurate, valuable, and useful; in others, it is inaccurate, misleading, and false.

§ 344. Free, Combined, and Colloidal Silica.

If the clay under investigation contains colloidal silica, most of this will pass into solution when the clay is digested with hydrochloric acid, and all will dissolve when the argillaceous matter is determined. Colloidal silica, if not separately determined, will then be reported with the argillaceous matter.[2] Some consider that a small quantity of colloidal silica has an important influence on the working properties of the clay. This question, however, is not, at present, under discussion.

The Determination of Colloidal Silica.—The colloidal silica in a clay can be determined by digesting 2 grms. of the sample with 100 c.c. of a 5 per cent. solution of sodium carbonate in a platinum dish on a water bath for about an hour. Decant off the clear,[3] and repeat the treatment with a fresh solution. Filter and wash with a hot dilute solution of sodium carbonate. Add an excess of hydrochloric acid to the filtrate; evaporate to dryness, and separate the silica as described on page 167. Or, the residue can be washed, dried, and weighed—the "loss" represents the matter removed by the sodium carbonate treatment.[4] In the latter case, much of the "colloidal" alumina would dissolve and be reported with "colloidal silica."

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[1] A. Leopold, *Magyar Chem. Folyoirait*, **11**. 177, 1905; H. Bollenbach, *Chem. Ind.*, **31**. 445, 1908; *Sprech.*, **41**. 340, 351, 1908; E. Greiner, *ib.*, **42**. 399, 413, 1909.

[2] W. H. Zimmer, *Trans. Amer. Cer. Soc.*, **3**. 25, 1901; F. G. Pence, *ib.*, **12**. 43, 1910. A. Hambloch (*Chem. Ztg.*, **36**. 1058, 1912) uses a 5 per cent. sodium hydroxide solution.

[3] Care must be taken in filtration, since small particles of clay may pass through ordinary filter papers.

[4] R. Fresenius, *Journ. prakt. Chem.* (1), **57**. 65, 1852; *Anleitung zur quantitativen chemischen Analyse*, Braunschweig; Eng. trans., London, **2**. 269, 1900; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **176**. 109, 1900; F. H. Hatch, *Tschermak's Mitt.*, **7**. 308, 1886; A. J. J. Browne and J B. Harrison, *cit.* page 525; F. G. Pence, *Trans. Amer. Cer. Soc.*, **12**. 43, 1910.

The Results.—It is advisable to run a blank experiment, and to keep the stock solution of sodium carbonate in a cerasine bottle, because, as previously indicated, a solution of sodium carbonate removes silica, etc., from glass and porcelain vessels. To illustrate the results obtained by this process the following determinations are cited (all but the first number have been corrected by subtracting the "correction factor" 0·02):

	Per cent. dissolved.
Blank experiment (or correction factor)	0·02
Silicic acid (precipitated and dried at 110°)	100·00
Silicic acid (ignited 20 minutes on blast)	75·62
Quartz (rock crystal)—coarse (page 664)[1]	0·11
Quartz (rock crystal)—fine (page 664)[1]	1·23
Quartz sand (ignited 20 minutes on blast)[1]	1·78
Altofts shale	1·48
Glenboig clay	2·08
Halloysite (Vigoux, Indre)	10·58

If no allowance is made, there is therefore a small error due to the action of the sodium carbonate solution on quartz. We are not sure if the sodium carbonate removes all the colloidal silica. The error is much greater if the sodium carbonate solution be mixed with sodium hydroxide, as in, say, Lunge's solution.

Other Methods.—Sjollema[2] claims that far more accurate results are obtained by boiling the sample with a 33 per cent. aqueous solution of diethylamine. Apart from the cost of the reagent, and the fact that the solution "bumps" badly when boiling, rather poor results have been obtained in my laboratory with this process. Hermann[3] recommends boiling the clay with a 0·1 per cent. solution of potassium paratungstate. When 10 c.c. of the solution are afterwards treated with 1 c.c. of an aqueous solution of sodium acetate[4] and 3 drops of a 5 per cent. solution of cæsium chloride, a crystalline precipitate is obtained if colloidal silica be present. The process has not proved satisfactory when it is applied quantitatively. In the absence of phosphoric acid, the molybdate process (page 603) can sometimes be used for estimating the amount of silica in the extract from the clay.

Free and Combined Silica.—Some analysts apply the term *combined silica* to the silica present in that portion of a clay which is decomposed by the sulphuric acid treatment; and the term *free silica* to the silica present in that portion of the clay which is not decomposed by the sulphuric acid treatment. The idea seems to be that the clay is composed of kaolinite and sand or quartz; that kaolinite alone is broken down by the sulphuric acid treatment; and that the insoluble matter is sand or free silica.[5] All three assumptions are erroneous. Further, the insoluble residue includes various silicates—felspar, mica, hornblende, etc.—and in these silicates, the silica, SiO_2, is just as much "combined" as that combined in the kaolinite. Hence, the objections urged against the system of rational analysis might also be advanced here; and Ries rightly argues that the custom of reporting the "silica" as "free silica" and "combined silica" should be dropped, because the terms are misleading.[6]

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[1] According to R. Schwarz (*Zeit. anorg. Chem.*, **76**. 422, 1912), when grains 0·04 mm. in diameter are boiled for half an hour with a 5 per cent. solution of sodium carbonate, 2·11 per cent. of quartz dissolves; and 2·77 per cent. of tridymite.

[2] B. Sjollema, *Journ. Landw. Chem.*, **50**. 371, 1902.

[3] H. Hermann, *Zeit. anal. Chem.*, **46**. 318, 1907.

[4] Dissolve 15 grms. of crystalline sodium acetate in 35 grms. of water, and 5 grms. of glacial acetic acid.

[5] See T. E. Thorpe, *Quantitative Chemical Analysis*, London, 184, 1883.

[6] H. Ries, *Clays—their Occurrence, Properties, and Uses*, New York, 68, 1906.

§ 345. The Composition of Felspathic and Quartz Detritus.

We next investigate the composition of the residue left after the clay substance has been removed. Following Seger, it is generally assumed that the residue is unweathered felspar or felspathic minerals and quartz. This assumption, in many cases, has no experimental foundation. For instance, felspar is seldom, if ever, found in the china clay from Cornwall or Devonshire, and yet half the residue in these clays would be reported as felspar by the method of rational analysis. Hussak, also, found no felspar in the majority of the kaolins he examined.[1] In spite of this, it is by no means uncommon to find ball and china clays reported with *n* per cent. of felspar when none is present.

The felspathic residue will include all those minerals which resist, wholly or in part, the sulphuric acid treatment. Again, practically all the siliceous minerals are decomposed by hydrofluoric acid, but, as indicated on page 657, a few less important minerals will escape that acid, and, in consequence, these will be included with "quartz *débris*."

Again, the mixed precipitate of aluminium and iron hydroxides is supposed to be alumina, and, on that assumption, its weight is multiplied by 5·45 —the amount of potash felspar corresponding with one part of alumina. Usually, a part of the potash is replaced by soda in the ideal potash felspar, and a part of the aluminium by iron. Both these factors make the above ratio deviate from 5·451. Seger used 5·41. Bollenbach[2] determines the ferric oxide separately and subtracts it from the "ammonia precipitate" before calculating the $Al_2O_3 . 2SiO_2 . 2H_2O$ from the alumina. Others[3] have multiplied the amount of alumina by 9, or by 8·5, and called the felspathic detritus "mica." We have seen on page 663 that a part of the mica in the clay may appear with the argillaceous matter, and part with the felspathic detritus. In consequence, there is some uncertainty as to the nature of the minerals which make up the residue from the sulphuric acid treatment.

It is seldom possible to make a quantitative estimate from the microscopic examination of the clay, because: (1) The minerals are often covered with a more or less opaque weathered crust which prevents an application of the optical tests; and (2) The mineral grains are often too small to permit satisfactory optical tests.[4] Hence, the method of rational analysis has received but little, if any, aid from the microscope (see Vol. II.).

§ 346. The Ultimate and Rational Analyses.

Some have been so strongly impressed with the difficulties involved in conducting a satisfactory rational analysis that they have abandoned the operation,[5] and calculated the supposed mineral composition by a process similar to that which follows:—

Let it be required to calculate the proportion of the three components (1)

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[1] E. Hussak, *Sprech.*, **22.** 8, 1889.

[2] H. Bollenbach, *Sprech.*, **41.** 340, 351, 1908.

[3] A. E. Tucker (*The Great Western Railway Co. v. The Carpella United China Clay Co. Ltd.*, 175, 1908) and R. R. Tatlock (*The North British Railway Co. v. Turners Ltd.*, 74, 1904) consider calculating the alkalies to felspar to be the "fairest and best" way. Obviously, if we are satisfied with guessing, either way may be taken. See also W. C. Hancock, *Journ. Soc. Chem. Ind.*, **29.** 309, 1910.

[4] Thus, a most experienced mineralogist reported that he was unable to say for certain whether some of the finer grains in the above-mentioned shale were mica or quartz. For the difficulty with mica and kaolinite, see J. W. Gregory, *The Great Western Railway Co. v. The Carpella United China Clay Co. Ltd.*, 324, 1908.

[5] E. R. Buckley, *Report on the Clays and the Clay Industries of Wisconsin*, Madison, Wis., 267, 1901. See also Heim, *Sprech.*, **28.** 519, 547, 1895.

kaolinite or clayite, (2) *felspar*, *and* (3) *quartz directly from the ultimate analysis.* Take Altofts shale in illustration. The ultimate analysis of the sample of Altofts shale, dried at 110°, previously cited, furnished:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Loss on ignition.
51·92	0·87	20·08	6·40	1·58	0·57	2·72	0·86	14·61

The loss on ignition included 4·42 per cent. of carbon, and 2·44 per cent. of carbon dioxide. It is required to calculate the proportion of kaolinite or clayite, felspar, and quartz on the assumption that the clay contains potash and soda felspars, quartz, and clayite or kaolinite. Several different ways are possible; not all are concordant.[1]

From the formulæ for potash ($K_2O.Al_2O_3.6SiO_2$) and soda ($Na_2O.Al_2O_3.6SiO_2$) felspar, it follows that the per cent. $K_2O \times 3·83$ represents the per cent. of silica in potash felspar; and the per cent. of $Na_2O \times 5·8$ represents the per cent. of silica in soda felspar. Hence, the amount of silica in the two felspars will be:

Potash felspar	3·83 × 2·72 = 10·42	per cent.
Soda felspar	5·8 × 0·86 = 4·99	,,
Total silica in the felspars	15·41	,,

Again, from the formulæ for the two felspars, the per cent. of potash multiplied by 1·09 represents the amount of alumina in potash felspar; and the per cent. of soda multiplied by 1·65 gives the corresponding amount of alumina in the soda felspar. Hence, the alumina in the two felspars will be:

Potash felspar	1·09 × 2·72 = 2·96	per cent.
Soda felspar	1·65 × 0·86 = 1·42	,,
Total alumina in the felspars	4·38	,,

The difference between the total alumina and the alumina in the felspars represents the alumina in the kaolinite; and the product of the alumina in the kaolinite with 1·18 represents the amount of silica combined as kaolinite. Hence

Alumina in clay	20·08	per cent.
Alumina in felspars	4·38	,,
Alumina in kaolinite	15·70	,,

The ferric oxide presents a difficulty. Is it to be ignored? Is it to be included with the "alumina"? Is it to be calculated as nontronite—$Fe_2O_3.2SiO_2.2H_2O$? Or is it to be included with the clay substance? With high-grade china clays there is no difficulty in answering the questions, because the amount of iron is negligibly small—so far as the degree of accuracy of the calculation is concerned. It is usually included either with the alumina or with the argillaceous matter,[2] generally the latter. As a matter of fact, in this particular sample most of the iron was removed by digestion with hydrochloric acid (1 : 1), and it should therefore be placed as a constituent by itself. The fact that the clay effervesced with evolution of carbon dioxide when treated with an acid proved that some constituents in the ultimate analysis were present as carbonate. The comparatively low proportion of CaO and MgO and the high proportion of "iron" pointed to the presence of ferrous carbonate. When the necessary calculation is made, we get: Amount of carbon dioxide × 1·64 = 2·44 × 1·64 = 4·0 per cent. of FeO; or

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[1] For instance, if we make an assumption about the composition of the mica, felspar, clayite, and quartz presumably in the clay, the method of calculation devised by J. W. Mellor, *Trans. Eng. Cer. Soc.*, 7. 117, 1908, can be employed after deducting the proper allowance for siderite and carbon.

[2] We have seen, page 658, that most of the iron in this particular shale was probably present as ferrous carbonate.

$4·0 + 2·44 =$ nearly 6·5 per cent. of ferrous carbonate. Hence, since: Amount $FeO \times \frac{10}{9} = 4·0 \times \frac{10}{9} = 4·44$ per cent. of ferric oxide; 6·4 less $4·4 = 2·0$ per cent. of ferric oxide remains unaccounted for. Again,

Silica with kaolinite (1·18 × 15·7)	18·53	per cent.
Silica with felspars	15·41	,,
Silica with kaolinite and felspars	33·94	,,
Total silica in clay	51·92	per cent.
Silica with kaolinite and felspars	33·94	,,
Silica as quartz	17·98	,,

Add up the percentage amounts of magnesia,[1] lime, and alkalies, with the computed amounts of silica and alumina for the felspars; and add up the loss on ignition (7·75), ferric oxide, and the computed alumina and silica for the kaolinite as argillaceous matters.[2] Summarising these results:

Argillaceous matter	Silica	18·5	44·0
	Alumina and iron oxide	17·7	
	Water	7·8	
Felspathic matter	Silica	15·4	25·5
	Alumina	4·4	
	Bases	6·0	
Quartz (silica)			18·0
Ferrous carbonate			6 4
Carbonaceous matter			4·4

A comparison of this with the actual result, as indicated in the table below, is not satisfactory. The discrepancy partly arises from the *dubious assumption* that the alkalies in the ultimate analysis all belong to felspathic matter, and none

Comparison of the Rational Composition of Altofts Shale estimated[3] by different Methods.

	Observed.	Computed from ultimate analysis of matter soluble and insoluble in sulphuric acid, etc.	Computed from ultimate analysis of whole clay.
Carbonaceous matter	4·4	4·4	4·4
Ferrous carbonate	6·4	6·4	6·4
Argillaceous matter	48·6	47·8	44·0
Felspathic detritus	5·4	6·6	25·5
Quartz *débris*	35·2	34·4	18·0

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[1] If calcium and magnesium carbonates were present, they would be removed by the hydrochloric acid treatment.

[2] The "loss on ignition" may be employed as a check on the work, since the product of the "loss on ignition" with 7·17 represents the corresponding amount of clayite or kaolinite. The "loss on ignition" is usually rather less than the corresponding amount of clayite, even if the amounts of carbonaceous matter and carbon dioxide be first deduced. There is a small error due to gain in weight by the oxidation of ferrous oxide. Some consider that a certain amount of alkali takes the place of H_2O in $Al_2O_3 . 2SiO_2 . 2H_2O$. C. F. Binns (*Trans. Amer. Cer. Soc.*, 8. 198, 1906) assumes that a little of the alkali is adsorbed by the argillaceous matter.

[3] Note the distinction between *to estimate* and *to determine* in analytical work. The former means "to judge or form an opinion from imperfect data"; the latter, "to ascertain by definite measurement." Sometimes it is difficult to decide where to draw the line—*e.g.* soda, pages 238–9; and sometimes an estimation is more accurate than a determination. However, the distinction has been emphasised in the Courts.

to micaceous and argillaceous matters. The method here outlined generally gives good results with high-grade clays, but with the low-grade clays, as with the rational analysis proper, the results are hopeless. Consequently, our attitude towards the method of calculation just indicated, and to the process of rational analysis, is largely determined by the particular type of clay under consideration, and the purpose for which the estimation is made. With the high-grade clays, the margin of error is small; with low-grade clays (and possibly with Cornish stone), we can say with Bischof[1] the process is "worthless" (*wertlos*), and with Prössel, "useless" (*unbrauchbar*).

We must here confess our inability to prescribe a process of chemical analysis of general applicability which will enable us to deduce the exact mineralogical composition of clays. *Blind faith in the routine process is sure to err.* A certain amount of judgment must be exercised in adapting a process of analysis to particular clays and to particular methods of manufacture. We must decide what minerals are technically important, and a process must be devised to deal with them, not necessarily to furnish the highest degree of accuracy, but rather to serve as a guide for the best treatment of the clay to furnish the desired results. One example will suffice.

Zschokke's Method of Rational Analysis.—Zschokke[2] found the following combined mechanical and chemical process best suited his requirements:

(1) Boil 50 grms. of the dry clay for half an hour in a porcelain dish with water, and restore the water lost by evaporation from time to time. After standing 24 hours, wash the clay on a sieve 8570 Continental mesh (say, 240 British mesh) until the washings flow through clear. Break up any lumps by rubbing on the sieve, or between the fingers, or, if necessary, on a glass plate with a rubber pestle. The residue on the sieve consists of quartz, felspar, gypsum, pyrites, etc. Dry at 110°, and weigh.

(2) The residue on the sieve is treated with dilute hydrochloric acid (1 : 10) and washed until the washings show no lime reaction. Filter, dry and weigh the residue. The residual substance from (1) gives the coarse-grained calcium and magnesium carbonates, gypsum, and iron oxide.

(3) The washings are evaporated to dryness and weighed as in (1). The result is fine-grained quartz, felspar, calcium and magnesium carbonates, gypsum, pyrites, etc.

(4) Treat the residue from (3) as described under (2). The results are subtracted from (3) and give fine-grained gypsum, felspar, quartz.

The results are expressed in percentages:

I. Non-plastic constituents			38·6
A. Coarse-grained constituents		13·9	
(*a*) Quartz, felspar	7·8		
(*b*) $CaCO_3$ and $MgCO_3$	6·1		
B. Fine-grained constituents		24·7	
(*a*) Quartz, felspar	11·3		
(*b*) $CaCO_3$ and $MgCO_3$	13·4		
II. Clay substance (by difference)			61·4

The clays treated by this method were required for bricks fired at too low a temperature for the felspar and quartz to play a particularly important part during the firing. Information about the size of grain of the non-plastic constituents, and the amount of the calcium and magnesium carbonates present in the clay, was particularly desired. Hence a justification of Zschokke's procedure.

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[1] C. Bischof, *Die feuerfesten Tone*, Leipzig, 103, 1904; B. P. Tenax (B. Prössel), *Die Steingut und Porzellanfabrikation*, Leipzig, 8, 1879.

[2] B. Zschokke, *Baumaterialienkunde*, 7. 165, 1902; *Mitt. Eidg. Materialpruf. Anstalt*, Zurich, **11**. 22, 1907.

§ 347. Are the Ultimate and Rational Analyses Consistent?

The ultimate and rational analyses of the high-grade clays, that is, clays containing a large proportion of kaolinite or clayite, usually agree very well. With these clays the proportion of felspar and quartz detritus is small. Consequently, the errors arising from secondary reactions in the removal of clay substance are relatively small. For instance, if a clay has 70 per cent. of argillaceous matter, 4 per cent. of felspar, and 26 per cent. of quartz, even if 20 per cent. of the felspar breaks down by the sulphuric acid treatment, it would only have the effect of diminishing the proportion of felspar 0·8 per cent., and of raising the clay substance accordingly. If two clays contain the same minerals, and if the sulphuric acid attacks both in the same way, the ultimate and rational analyses must necessarily agree. Disagreement can only occur when the clays contain different minerals, the same minerals in different proportions or in different states of subdivision. Cases have been recorded which apparently contradict this observation. For example:[1]

ULTIMATE ANALYSES.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	$\underbrace{K_2O, Na_2O}$.	Loss on ignition.
A . .	62·40	26·51	1·14	0·01	0·57	0·98	8·80
B . .	62·52	25·57	0·92	0·10	0·65	1·04	9·27
C . .	59·30	27·17	1·44	nil.	0·48	0·52	9·67

RATIONAL ANALYSES.

	Clay substance.	Felspar.	Quartz.
A	66·33	18·91	15·61
B	72·05	0·10	27·76
C	43·74	36·84	19·42

In A the proportion alkalies to felspar is 1 : 18. I am not acquainted with a felspar with alkalies and felspar in these proportions (by weight). Albite has this ratio nearly as 1 : 9; and orthoclase, 1 : 6. There is obviously something wrong. The case is much worse with the C clay, for it is at once obvious that 0·52 per cent. of alkalies is quite incompatible with 36·8 per cent. of felspar. See also page 672. This sort of thing is not at all uncommon,[2] although I have not met such bad examples in my own practice. We are thus driven to conclude that the method gives incompatible results, or the analyses are at fault. We naturally inquire: Was the clay substance all decomposed by the sulphuric acid treatment in the rational analysis of clays A and C? Was some of the felspar decomposed by the sulphuric acid in the rational analysis of the B clay?

Summary.—Here, then, it is inferred that the method for conducting the rational analysis gives results incompatible with the ultimate analysis; the ultimate analysis can be conducted with a great degree of precision; hence the process of rational analysis cannot be recommended as a general method for comparing the properties of the different types of clay, although, as indicated above, the rational analysis is useful (1) for comparing the properties of high-grade clays which do not differ very materially in the nature of their constituent minerals; and (2) it is sometimes a help in forming a rough idea what minerals are present in clays.[3] In the former case, however, the "rational composition" can be computed accurately enough from the ultimate analysis.

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[1] A is a raw china clay from North Carolina—H. Ries, *North Carolina Geol. Sur.*, **13**. 62, 1897; B is a slip clay from Löthian, Saxony—H. A. Seger, *Tonind. Ztg.*, **16**. 1031, 1892; and C clay is from Shropshire—J. T. Norman, *Report on some Shropshire Clays*, London, 1903.

[2] J. W. Mellor, *Pot. Gaz.*, **35**. 1060, 1908; H. Ries, *Trans. Amer. Inst. Min. Eng.*, **28**. 160, 1899.

[3] Or rather the fractional separation of constituents soluble in certain menstrua.

APPENDIX.

> The human mind is seldom satisfied, and is certainly never exercising its highest functions when it is doing the work of a calculating machine.—J. C. MAXWELL.

THE results of old arithmetical operations most frequently required are registered in the form of tables. The use of such tables not only prevents the wasting of time and energy on a repetition of old operations, but also conduces to more accurate work, since there is less liability to error once accurate tables have been compiled.

The specific gravity-concentration tables—Tables LXXIV. to LXXXIII.—explain themselves. They are referred to in different parts of this book. The authority for each is indicated in the text. Table LXXXV. *et seq.* are used like the ordinary reference logarithm tables. For instance, at 13·8° the vapour pressure of water is equivalent to a 11·84 mm. column of mercury.

Tables LXXXVI. to XCIV. have been specially computed for this book. They are used in the ordinary manner. For instance, page 236, a precipitate of potassium chloroplatinate weighing 0·0547 grm. will, from Table LXXXVI., be equivalent to 0·0168 grm. of potassium chloride ; and, from Table LXXXVIII., to 0·0106 grm. of potash, K_2O. From Table LXXXIX., 0·0059 grm. of sodium chloride is equivalent to 0·0031 grm. of soda, Na_2O. Similarly, page 238, Table LXXXVII. tells us that 0·0272 grm. of potassium perchloride is equivalent to 0·0146 grm. of potassium chloride, and the latter, from Table LXXXVIII., is equivalent to 0·0092 grm. of potash, K_2O. The other tables are to be used in an analogous manner.

Table LXXIV.—Sulphuric Acid—Specific Gravity and Concentration.

G. Lunge and M. Isler, *Zeit. angew. Chem.*, 3. 129, 1890; G. Lunge, *Technical Chemists' Handbook*, London, 1910.

Specific Gravity 15°.	100 parts by weight contain		Kilo per litre.	Specific Gravity 15°.	100 parts by weight contain		Kilo per litre.
	SO_3.	H_2SO_4.	H_2SO_4.		SO_3.	H_2SO_4.	H_2SO_4.
1·010	1·28	1·57	0·016	1·305	32·46	39·77	0·519
1·020	2·47	3·03	0·031	1·310	32·94	40·35	0·529
1·030	3·67	4·49	0·046	1·315	33·41	40·93	0·538
1·040	4·87	5·96	0·062	1·320	33·88	41·50	0·548
1·050	6·02	7·37	0·077	1·325	34·35	42·08	0·557
1·060	7·16	8·77	0·093	1·330	34·80	42·66	0·567
1·070	8·32	10·19	0·109	1·335	35·27	43·20	0·577
1·080	9·47	11·60	0·125	1·340	35·71	43·74	0·586
1·090	10·60	12·99	0·142	1·345	36·14	44·28	0·596
1·100	11·71	14·35	0·158	1·350	36·58	44·82	0·605
1·110	12·82	15·71	0·175	1·355	37·02	45·35	0·614
1·120	13·89	17·01	0·191	1·360	37·45	45·88	0·624
1·130	14·95	18·31	0·207	1·365	37·89	46·41	0·633
1·140	16·01	19·61	0·223	1·370	38·32	46·94	0·643
1·150	17·07	20·91	0·239	1·375	38·75	47·47	0·653
1·160	18·11	22·19	0·257	1·380	39·18	48·00	0·662
1·170	19·16	23·47	0·275	1·385	39·62	48·53	0·672
1·180	20·21	24·76	0·292	1·390	40·05	49·06	0·682
1·190	21·26	26·04	0·310	1·395	40·48	49·59	0·692
1·200	22·30	27·32	0·328	1·400	40·91	50·11	0·702
1·205	22·82	27·95	0·337	1·405	41·33	50·63	0·711
1·210	23·33	28·58	0·346	1·410	41·76	51·15	0·721
1·215	23·84	29·21	0·355	1·415	42·17	51·66	0·730
1·220	24·36	29·84	0·364	1·420	42·57	52·15	0·740
1·225	24·88	30·48	0·373	1·425	42·96	52·63	0·750
1·230	25·39	31·11	0·382	1·430	43·36	53·11	0·759
1·235	25·88	31·70	0·391	1·435	43·75	53·59	0·769
1·240	26·35	32·28	0·400	1·440	44·14	54·07	0·779
1·245	26·83	32·86	0·409	1·445	44·53	54·55	0·789
1·250	27·29	33·43	0·418	1·450	44·92	55·03	0·798
1·255	27·76	34·00	0·426	1·455	45·31	55·50	0·808
1·260	28·22	34·57	0·435	1·460	45·69	55·97	0·817
1·265	28·69	35·14	0·444	1·465	46·07	56·43	0·827
1·270	29·15	35·71	0·454	1·470	46·45	56·90	0·837
1·275	29·62	36·29	0·462	1·475	46·83	57·37	0·846
1·280	30·10	36·87	0·472	1·480	47·21	57·83	0·856
1·285	30·57	37·45	0·481	1·485	47·57	58·28	0·866
1·290	31·04	38·03	0·490	1·490	47·95	58·74	0·876
1·295	31·52	38·61	0·500	1·495	48·34	59·22	0·886
1·300	31·99	39·19	0·510	1·500	48·73	59·70	0·896

Table LXXIV.—*continued.*

Specific Gravity 15°.	100 parts by weight contain		Kilo per litre.
	SO_3.	H_2SO_4.	H_2SO_4.
1·505	49·12	60·18	0·906
1·510	49·51	60·65	0·916
1·515	49·89	61·12	0·926
1·520	50·28	61·59	0·936
1·525	50·66	62·06	0·946
1·530	51·04	62·53	0·957
1·535	51·43	63·00	0·967
1·540	51·78	63·43	0·977
1·545	52·12	63·85	0·987
1·550	52·46	64·26	0·996
1·555	52·79	64·67	1·006
1·560	53·22	65·20	1·017
1·565	53·59	65·65	1·027
1·570	53·95	66·09	1·038
1·575	54·32	66·53	1·048
1·580	54·65	66·95	1·058
1·585	55·03	67·40	1·068
1·590	55·37	67·83	1·078
1·595	55·73	68·26	1·089
1·600	56·09	68·70	1·099
1·605	56·44	69·13	1·110
1·610	56·79	69·56	1·120
1·615	57·15	70·00	1·131
1·620	57·49	70·42	1·141
1·625	57·84	70·85	1·151
1·630	58·18	71·27	1·162
1·635	58·53	71·70	1·172
1·640	58·88	72·12	1·182
1·645	59·22	72·55	1·193
1·650	59·57	72·96	1·204
1·655	59·92	73·40	1·215
1·660	60·26	73·81	1·225
1·665	60·60	74·24	1·236
1·670	60·95	74·66	1·246
1·675	61·29	75·08	1·259
1·680	61·63	75·50	1·268
1·685	61·93	75·86	1·278
1·690	62·29	76·30	1·289
1·695	62·64	76·73	1·301
1·700	63·00	77·17	1·312
1·705	63·35	77·60	1·323
1·710	63·70	78·04	1·334
1·715	64·07	78·48	1·346
1·720	64·43	78·92	1·357
1·725	64·78	79·36	1·369
1·730	65·14	79·80	1·381
1·735	65·50	80·24	1·392
1·740	65·86	80·68	1·404
1·745	66·22	81·12	1·416
1·750	66·58	81·56	1·427
1·755	66·94	82·00	1·439
1·760	67·30	82·44	1·451
1·765	67·76	83·01	1·465
1·770	68·17	83·41	1·478
1·775	68·60	84·02	1·491
1·780	68·98	84·50	1·504
1·785	69·47	85·10	1·519
1·790	69·96	85·70	1·534
1·795	70·45	86·30	1·549
1·800	70·96	86·92	1·565
1·805	71·50	87·60	1·581
1·810	72·08	88·30	1·598
1·815	72·69	89·05	1·621
1·820	73·51	90·05	1·639
1·821	73·63	90·20	1·643
1·822	73·80	90·40	1·647
1·823	73·96	90·60	1·651
1·824	74·12	90·80	1·656
1·825	74·29	91·00	1·661
1·826	74·49	91·25	1·666
1·827.	74·69	91·50	1·671
1·828	74·86	91·70	1·676
1·829	75·03	91·90	1·681
1·830	75·19	92·10	1·685
1·831	75·46	92·43	1·692
1·832	75·69	92·70	1·698
1·833	75·89	92·97	1·704
1·834	76·12	93·25	1·710
1·835	76·35	93·56	1·717
1·836	76·57	93·80	1·722
1·837	76·90	94·20	1·730
1·838	77·23	94·60	1·739
1·839	77·55	95·00	1·748
1·840	78·04	95·60	1·759
1·8405	78·33	95·95	1·765
1·8410	78·69	96·30	1·784
1·8415	79·47	97·35	1·792
1·8410	80·16	98·20	1·808
1·8405	80·43	98·52	1·814
1·8400	80·59	98·72	1·816
1·8395	80·63	98·77	1·817
1·8390	80·93	99·12	1·823
1·8385	81·08	99·31	1·826

Table LXXV.—Nitric Acid—Specific Gravity and Concentration.

G. Lunge and H. Rey, *Zeit. angew. Chem.*, 4. 165, 1891 ; G. Lunge, *Technical Chemists' Handbook*, London, 1910.

Specific Gravity 15°.	Percentage by weight.		Grams per litre.		Specific Gravity 15°.	Percentage by weight.		Grams per litre.	
	N_2O_5.	HNO_3.	N_2O_5.	HNO_3.		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·000	0·08	0·10	1	1	1·200	27·74	32·36	333	388
1·005	0·85	1·00	8	10	1·205	28·36	33·09	342	399
1·010	1·62	1·90	16	19	1·210	28·99	33·82	351	409
1·015	2·39	2·80	24	28	1·215	29·61	34·55	360	420
1·020	3·17	3·70	33	38	1·220	30·24	35·28	369	430
1·025	3·94	4·60	40	47	1·225	30·88	36·03	378	441
1·030	4·71	5·50	49	57	1·230	31·53	36·78	387	452
1·035	5·47	6·38	57	66	1·235	32·17	37·53	397	463
1·040	6·22	7·26	64	75	1·240	32·82	38·29	407	475
1·045	6·97	8·13	73	85	1·245	33·47	39·05	417	486
1·050	7·71	8·99	81	94	1·250	34·13	39·82	427	498
1·055	8·43	9·84	89	104	1·255	34·78	40·58	437	509
1·060	9·15	10·68	97	113	1·260	35·44	41·34	447	521
1·065	9·87	11·51	105	123	1·265	36·09	42·10	457	533
1·070	10·57	12·33	113	132	1·270	36·75	42·87	467	544
1·075	11·27	13·15	121	141	1·275	37·41	43·64	477	556
1·080	11·96	13·95	129	151	1·280	38·07	44·41	487	568
1·085	12·64	14·74	137	160	1·285	38·73	45·18	498	581
1·090	13·31	15·33	145	169	1·290	39·39	45·95	508	593
1·095	13·99	16·32	153	179	1·295	40·05	46·72	519	605
1·100	14·67	17·11	161	188	1·300	40·71	47·49	529	617
1·105	15·34	17·89	170	198	1·305	41·37	48·26	540	630
1·110	16·00	18·67	177	207	1·310	42·06	49·07	551	643
1·115	16·67	19·45	186	217	1·315	42·76	49·89	562	656
1·120	17·34	20·23	195	227	1·320	43·47	50·71	573	669
1·125	18·00	21·00	202	236	1·325	44·17	51·53	585	683
1·130	18·66	21·77	211	246	1·330	44·89	52·37	597	697
1·135	19·32	22·54	219	256	1·335	45·62	53·22	609	710
1·140	19·98	23·31	228	266	1·340	46·35	54·07	621	725
11·45	20·64	24·08	237	276	1·345	47·08	54·93	633	739
1·150	21·29	24·84	245	286	1·350	47·82	55·79	645	753
1·155	21·94	25·60	254	296	1·355	48·57	56·66	658	768
1·160	22·60	26·36	262	306	1·360	49·35	57·57	671	783
1·165	23·25	27·12	271	316	1·365	50·13	58·48	684	798
1·170	23·90	27·88	279	326	1·370	50·91	59·39	698	814
1·175	24·54	28·63	288	336	1·375	51·69	60·30	711	829
1·180	25·18	29·38	297	347	1·380	52·52	61·27	725	846
1·185	25·83	30·13	306	357	1·385	53·35	62·24	739	862
1·190	26·47	30·88	315	367	1·390	54·20	63·23	753	879
1·195	27·10	31·62	324	378	1·395	55·07	64·25	768	896

Table LXXV.—*continued.*

Specific Gravity 15°.	Percentage by weight.		Grams per litre.		Specific Gravity 15°.	Percentage by weight.		Grams per litre.	
	N_2O_5.	HNO_3.	N_2O_5.	HNO_3.		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·400	55·97	65·30	783	914	1·465	69·79	81·42	1023	1193
1·405	56·92	66·40	800	933	1·470	71·06	82·90	1045	1219
1·410	57·86	67·50	816	952					
1·415	58·83	68·63	832	971	1·475	72·39	84·45	1068	1246
1·420	59·83	69·80	849	991	1·480	73·76	86·05	1092	1274
1·425	60·84	70·98	867	1011	1·485	75·18	87·70	1116	1302
1·430	61·86	72·17	885	1032	1·490	76·80	89·60	1144	1335
1·435	62·91	73·39	903	1053	1·495	78·52	91·60	1174	1369
1·440	64·01	74·68	921	1075	1·500	80·65	94·09	1210	1411
1·445	65·13	75·98	941	1098	1·505	82·63	96·39	1244	1451
1·450	66·24	77·28	961	1121	1·510	84·09	98·10	1270	1481
1·455	67·38	78·60	981	1144	1·515	84·92	99·07	1287	1501
1·460	68·56	79·98	1001	1168	1·520	85·44	99·67	1299	1515

Table LXXVI.—Hydrochloric Acid—Specific Gravity and Concentration.

G. Lunge and L. Marchlewski, *Zeit. angew. Chem.*, 4. 133, 1891 ; G. Lunge, *Technical Chemists' Handbook*, London, 1910.

Specific Gravity at $\frac{15°}{4°}$ in vacuo.	100 parts by weight correspond to parts by weight of HCl.	1 litre contains g. of HCl.	Specific Gravity at $\frac{15°}{4°}$ in vacuo.	100 parts by weight correspond to parts by weight of HCl.	1 litre contains g. of HCl.
1·000	0·16	1·6	1·105	20·97	232
1·005	1·15	12	1·110	21·92	243
1·010	2·14	22	1·115	22·86	255
1·015	3·12	32	1·120	23·82	267
1·020	4·13	42	1·125	24·78	278
1·025	5·15	53			
1·030	6·15	64	1·130	25·75	291
1·035	7·15	74	1·135	26·70	303
1·040	8·16	85	1·140	27·66	315
1·045	9·16	96	1·145	28·61	328
1·050	10·17	107	1·150	29·57	340
1·055	11·18	118	1·155	30·55	353
1·060	12·19	129	1·160	31·52	366
1·065	13·19	141	1·165	32·49	379
1·070	14·17	152	1·170	33·46	392
1·075	15·16	163	1·175	34·42	404
1·080	16·15	174	1·180	35·39	418
1·085	17·13	186	1·185	36·31	430
1·090	18·11	197	1·190	37·23	443
1·095	19·06	209	1·195	38·16	456
1·100	20·01	220	1·200	39·11	469

Table LXXVII.—Hydrobromic Acid—Specific Gravity and Concentration.

H Topsoe, *Ber.*, 3. 404, 1870.

Per cent. HBr.	0	1	2	3	4	5	6	7	8	9
0	..	1·007	1·014	1·021	1·028	1·035	1·043	1·050	1·058	1·065
1	1·073	1·081	1·089	1·097	1·106	1·114	1·122	1·131	1·140	1·149
2	1·158	1·167	1·176	1·186	1·196	1·206	1·215	1·225	1·235	1·246
3	1·257	1·268	1·279	1·290	1·302	1·314	1·326	1·358	1·351	1·363
4	1·376	1·389	1·403	1·417	1·431	1·445	1·459	1·475	1·487	1·502

Table LXXVIII.—Hydrofluoric Acid—Specific Gravity and Concentration.

F. Winteler, *Zeit. angew. Chem.*, 15. 33, 1902.

	0	1	2	3	4	5	6	7	8	9
0	..	1·003	1·007	1·011	1·014	1·018	1·023	1·027	1·030	1·035
1	1·038	1·041	1·045	1·049	1·052	1·055	1·059	1·062	1·066	1·069
2	1·072	1·076	1·079	1·082	1·086	1·089	1·092	1·095	1·098	1·101
3	1·104	1·106	1·119	1·112	1·114	1·117	1·120	1·122	1·125	1·127
4	1·130	1·133	1·136	1·138	1·141	1·143	1·146	1·149	1·152	1·157

Table LXXIX.—Phosphoric Acid—Specific Gravity and Concentration.

H. Hager, *Commentar zur Pharmacopœia germanica*, Berlin, 1884.

Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.	Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.	Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.
1·809	68·0	93·67	1·661	59·0	81·28	1·521	50·0	68·88
1·800	67·5	92·99	1·653	58·5	80·59	1·513	49·5	68·19
1·792	67·0	92·30	1·645	58·0	79·90	1·505	49·0	67·50
1·783	66·5	91·61	1·637	57·5	79·21	1·498	48·5	66·81
1·775	66·0	90·92	1·629	57·0	78·52	1·491	48·0	66·12
1·766	65·5	90·23	1·621	56·5	77·83	1·484	47·5	65·43
1·758	65·0	89·54	1·613	56·0	77·14	1·476	47·0	64·75
1·750	64·5	88·85	1·605	55·5	76·45	1·469	46·5	64·06
1·741	64·0	88·16	1·597	55·0	75·77	1·462	46·0	63·37
1·733	63·5	87·48	1·589	54·5	75·08	1·455	45·5	62·68
1·725	63·0	86·79	1·581	54·0	74·39	1·448	45·0	61·99
1·717	62·5	86·10	1·574	53·5	73·70	1·441	44·5	61·30
1·709	62·0	85·41	1·566	53·0	73·01	1·435	44·0	60·61
1·701	61·5	84·72	1·599	52·5	72·32	1·428	43·5	59·92
1·693	61·0	84·03	1·551	52·0	71·63	1·422	43·0	59·23
1·685	60·5	83·34	1·543	51·5	70·94	1·415	42·5	58·55
1·677	60·0	82·65	1·536	51·0	70·26	1·409	42·0	57·86
1·669	59·5	81·97	1·528	50·5	69·57	1·402	41·5	57·17

Table LXXIX.—*continued.*

Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.	Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.	Sp. gr.	Per cent. P_2O_5.	Per cent. H_3PO_4.
1·396	41·0	56·48	1·249	28·0	38·57	1·122	15·0	20·66
1·389	40·5	55·79	1·244	27·5	37·88	1·118	14·5	19·97
1·383	40·0	55·10	1·239	27·0	37·19	1·113	14·0	19·28
1·377	39·5	54·41	1·233	26·5	36·50	1·109	13·5	18·00
1·371	39·0	53·72	1·228	26·0	35·82	1·104	13·0	17·91
1·365	38·5	50·34	1·223	25·5	35·13	1·110	12·5	17·22
1·359	38·0	52·35	1·218	25·0	34·44	1·096	12·0	16·53
1·354	37·5	51·66	1·213	24·5	33·75	1·091	11·5	15·84
1·348	37·0	50·97	1·208	24·0	33·06	1·087	11·0	15·15
1·342	36·5	50·28	1·203	23·5	32·37	1·083	10·5	14·46
1·336	36·0	49·59	1·198	23·0	31·68	1·079	10·0	13·77
1·330	35·5	48·90	1·193	22·5	30·99	1·074	9·5	13·09
1·325	35·0	48·21	1·188	22·0	30·31	1·070	9·0	12·40
1·319	34·5	47·52	1·183	21·5	29·62	1·066	8·5	11·71
1·314	34·0	46·84	1·178	21·0	28·93	1·062	8·0	11·02
1·308	33·5	46·15	1·174	20·5	28·24	1·058	7·5	10·33
1·303	33·0	45·46	1·169	20·0	27·55	1·053	7·0	9·64
1·298	32·5	44·77	1·164	19·5	26·86	1·049	6·5	8·95
1·292	32·0	44·08	1·159	19·0	26·17	1·045	6·0	8·26
1·287	31·5	43·39	1·155	18·5	25·48	1·041	5·5	7·57
1·281	31·0	42·70	1·150	18·6	24·80	1·037	5·0	6·89
1·276	30·5	42·01	1·145	17·5	24·11	1·033	4·5	6·20
1·271	30·0	41·33	1·140	17·0	23·42	1·029	4·0	5·51
1·265	29·5	40·64	1·135	16·5	22·73	1·025	3·5	4·82
1·260	29·0	39·95	1·130	16·0	22·04	1·021	3·0	4·13
1·225	28·5	39·26	1·126	15·5	21·35	1·017	2·5	3·44

Table LXXX.—Perchloric Acid.—Specific Gravity and Concentration.

K. van Emster, *Zeit. anorg. Chem.*, 52. 270, 1907.

At 15° (Water at 4° unity).

Sp. gr.	Per cent. $HClO_4$.	Sp. gr.	Per cent. $HClO_4$.	Sp. gr.	Per cent. $HClO_4$.	Sp. gr.	Per cent. $HClO_4$.
1·005	1·00	1·090	14·56	1·175	26·20	1·260	36·03
1·010	1·90	1·095	15·28	1·180	26·82	1·265	36·56
1·015	2·77	1·100	16·00	1·185	27·44	1·270	37·08
1·020	3·61	1·105	16·72	1·190	28·05	1·275	37·60
1·025	4·43	1·110	17·45	1·195	28·66	1·280	38·10
1·030	5·25	1·115	18·16	1·200	29·26	1·285	38·60
1·035	6·07	1·120	18·88	1·205	29·86	1·290	39·10
1·040	6·88	1·125	19·57	1·210	30·45	1·295	39·60
1·045	7·68	1·130	20·26	1·215	31·04	1·300	40·10
1·050	8·48	1·135	20·95	1·220	31·61	1·305	40·59
1·055	9·28	1·140	21·64	1·225	32·18	1·310	41·08
1·060	10·06	1·145	22·32	1·230	32·74	1·315	41·56
1·065	10·83	1·150	22·99	1·235	33·29	1·320	42·03
1·070	11·58	1·155	23·65	1·240	33·85	1·325	42·49
1·075	12·33	1·160	24·30	1·245	34·40	1·330	42·97
1·080	13·08	1·165	24·94	1·250	34·95	1·335	43·43
1·085	13·83	1·170	25·57	1·255	35·49	1·340	43·89

Table LXXX.—*continued.*

Sp. gr.	Per cent. $HClO_4$.	Sp. gr.	Per cent. $HClO_4$.	Sp. gr.	Per cent, $HClO_4$.	Sp. gr.	Per cent. $HClO_4$.
1·345	44·35	1·430	51·71	1·515	58·17	1·600	64·50
1·350	44·81	1·435	52·11	1·520	58·54	1·605	64·88
1·355	45·26	1·440	52·54	1·525	58·91	1·610	65·26
1·360	45·71	1·445	52·91	1·530	59·28	1·615	65·63
1·365	46·16	1·450	53·31	1·535	59·66	1·620	66·01
1·370	46·61	1·455	53·71	1·540	60·04	1·625	66·39
1·375	47·05	1·460	54·11	1·545	60·41	1·630	66·76
1·380	47·49	1·465	54·50	1·550	60·78	1·635	67·13
1·385	47·93	1·470	54·89	1·555	61·15	1·640	67·51
1·390	48·37	1·475	55·18	1·560	61·52	1·645	67·89
1·395	48·80	1·480	55·56	1·565	61·89	1·650	68·26
1·400	49·23	1·485	55·95	1·570	62·26	1·655	68·64
1·405	49·68	1·490	56·32	1·575	62·63	1·660	69·02
1·410	50·10	1·495	56·69	1·580	63·00	1·665	69·40
1·415	50·51	1·500	57·06	1·585	63·37	1·670	69·77
1·420	50·91	1·505	57·44	1·590	63·74	1·675	70·15
1·425	51·31	1·510	57·81	1·595	64·12		

Table LXXXI.—Formic Acid—Specific Gravity and Concentration.

G. M. Richardson and P. Alhaire, *Amer. Chem. Journ.*, 19. 149, 1897.

Sp. gr.	Grams formic acid per 100 grams of solution.									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	..	1·0020	1·0045	1·0071	1·0094	1·0116	1·0142	1·0171	1·0197	1·0222
1	1·0247	1·0272	1·0297	1·0322	1·0346	1·0371	1·0394	1·0418	1·0442	1·0465
2	1·0489	1·0513	1·0538	1·0562	1·0586	1·0610	1·0634	1·0657	1·0682	1·0706
3	1·0730	1·0754	1·0778	1·0801	1·0824	1·0848	1·0872	1·0896	1·0920	1·0941
4	1·0964	1·0991	1·1016	1·1039	1·1063	1·1086	1·1109	1·1131	1·1158	1·1186
5	1·1208	1·1224	1·1245	1·1270	1·1296	1·1321	1·1343	1·1362	1·1382	1·1402
6	1·1425	1·1449	1·1474	1·1494	1·1518	1·1544	1·1566	1·1585	1·1605	1·1629
7	1·1656	1·1678	1·1703	1·1729	1·1753	1·1770	1·1786	1·1802	1·1819	1·1838
8	1·1861	1·1877	1·1897	1·1915	1·1930	1·1954	1·1977	1·1995	1·2013	1·2029
9	1·2045	1·2060	1·2079	1·2100	1·2118	1·2141	1·2159	1·2171	1·2184	1·2203

Table LXXXII.—Acetic Acid.—Specific Gravity and Concentration.

A. C. Oudemans, *Zeit. Chem.* (2), 2. 750, 1866.

Per cent. Acetic Acid CH_3COOH.	0	1	2	3	4	5	6	7	8	9
0	0·9992	1·0007	1·0022	1·0037	1·0052	1·0067	1·0083	1·0098	1·0113	1·0127
1	1·0142	1·0157	1·0171	1·0185	1·0200	1·0214	1·0228	1·0242	1·0256	1·0270
2	1·0284	1·0298	1·0311	1·0324	1·0337	1·0350	1·0363	1·0375	1·0388	1·0400
3	1·0412	1·0424	1·0436	1·0447	1·0459	1·0470	1·0481	1·0492	1·0502	1·0513
4	1·0523	1·0533	1·0543	1·0552	1·0562	1·0571	1·0580	1·0589	1·0598	1·0607
5	1·0615	1·0623	1·0631	1·0638	1·0646	1·0653	1·0660	1·0666	1·0673	1·0679
6	1·0685	1·0691	1·0697	1·0702	1·0707	1·0712	1·0717	1·0721	1·0725	1·0729
7	1·0733	1·0737	1·0740	1·0742	1·0744	1·0746	1·0747	1·0748	1·0748	1·0748
8	1·0748	1·0747	1·0746	1·0744	1·0742	1·0739	1·0736	1·0731	1·0726	1·0720
9	1·0713	1·0705	1·0696	1·0686	1·0674	1·0660	1·0644	1·0625	1·0604	1·0580

Table LXXXIII.—Ammonia—Specific Gravity and Concentration.

G. Lunge and T. Wiernik, *Zeit. angew. Chem.*, 2. 182. 1889; G. Lunge, *Technical Chemists' Handbook*, London, 1910.

Sp. gr.	Per cent. NH_3.	Grms. NH_3 per 1000 c.c. at 15°.	Correction for temperature. ±1° from 13° to 17°.	Sp. gr.	Per cent. NH_3.	Grms. NH_3 per 1000 c.c. at 15°.	Correction for temperature. ±1° from 13° to 17°.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
9·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

Table LXXXIV.—Atomic Weights, International.

Names of Elements.	Symbols.	Approximate Atomic Weight.	International Atomic Weights. O = 16·00. H = 1·008.	Names of Elements.	Symbols.	Approximate Atomic Weight.	International Atomic Weights. O = 16·00. H = 1·008.
Aluminium	Al	27	27·1	Neodymium	Nd	144	144·3
Antimony	Sb	120	120·2	Neon	Ne	20	20·2
Argon	A	40	39·88	Nickel	Ni	59	58·68
Arsenic	As	75	74·96	Niobium (Columbium)	Nb Cb	93·5	93·5
Barium	Ba	137	137·37				
Beryllium (Glucinum)	Be Gl	9	9·1	Niton (radium emanation)	Nt	222·4	222·4
Bismuth	Bi	208	208·0	Nitrogen	N	14	14·01
Boron	B	11	11·0	Osmium	Os	191	190·9
Bromine	Br	80	79·92	**Oxygen**	**O**	**16**	**16**
Cadmium	Cd	112	112·4	Palladium	Pd	106	106·7
Caesium	Cs	133	132·81	Phosphorus	P	31	31·04
Calcium	Ca	40	40·07	Platinum	Pt	195	195·2
Carbon	C	12	12·00	Potassium	K	39	39·10
Cerium	Ce	140	140·25	Praseodymium	Pr	140·5	140·6
Chlorine	Cl	35·5	35·46	Radium	Ra	226·5	226·4
Chromium	Cr	52	52·0	Rhodium	Rh	103	102·9
Cobalt	Co	59	58·97	Rubidium	Rb	85	85·45
Copper	Cu	63·5	63·57	Ruthenium	Ru	101·5	101·7
Dysprosium	Dy	162·5	162·5	Samarium	Sm	150	150·4
Erbium	Er	167·5	167·5	Scandium	Sc	44	44·1
Europium	Eu	152	152·0	Selenium	Se	79	79·2
Fluorine	F	19	19·0	Silicon	Si	28	28·3
Gadolinium	Gd	157	157·3	Silver	Ag	108	107·88
Gallium	Ga	70	69·9	Sodium	Na	23	23·00
Germanium	Ge	72	72·5	Strontium	Sr	87·5	87·63
Gold	Au	197	197·2	Sulphur	S	32	32·07
Helium	He	4	3·99	Tantalum	Ta	181·5	181·5
Holmium	Ho	163·5	163·5	Tellurium	Te	127	127·5
Hydrogen	H	1	1·008	Terbium	Tb	159	159·2
Indium	In	115	114·8	Thallium	Tl	204	204·0
Iodine	I	127	126·92	Thorium	Th	232	232·4
Iridium	Ir	193	193·1	Thulium	Tm	168·5	168·5
Iron	Fe	56	55·85	Tin	Sn	118	119·0
Krypton	Kr	83	82·9	Titanium	Ti	48	48·1
Lanthanum	La	139	139·0	Tungsten	W	184	184·0
Lead	Pb	207	207·10	Uranium	U	238·5	238·5
Lithium	Li	7	6·94	Vanadium	V	51	51·0
Lutecium	Lu	174	174·0	Xenon	X	130	130·2
Magnesium	Mg	24	24·32	Ytterbium	Yb	172	172·0
Manganese	Mn	55	54·93	Yttrium	Y	89	89·0
Mercury	Hg	200	200·6	Zinc	Zn	65	65·37
Molybdenum	Mo	96	96·0	Zirconium	Zr	90·5	90·6

Table LXXXV.—The Vapour Pressure of Liquid Water at Different Temperatures in Millimetres of Mercury.

Based mainly on K. Scheel and W. Heuse, *Annalen der Physik* (4), **29**. 723, 1909 ; (4), **31**. 715, 1910.

Hydrogen Scale, Gravity Normal.

Temperature.	Millimetres of Mercury.									
	0	1	2	3	4	5	6	7	8	9
−4	3·40	3·38	3·35	3·33	3·30	3·28	3·26	3·23	3·21	3·18
−3	3·67	3·64	3·62	3·59	3·56	3·53	3·51	3·48	3·46	3·43
−2	3·95	3·92	3·89	3·87	3·84	3·81	3·78	3·75	3·72	3·70
−1	4·26	4·22	4·19	4·16	4·13	4·10	4·07	4·04	4·01	3·98
−0	4·58	4·55	4·51	4·48	4·45	4·41	4·38	4·35	4·32	4·29
+0	4·58	4·61	4·65	4·68	4·72	4·75	4·79	4·82	4·86	4·89
1	4·93	4·96	5·00	5·03	5·07	5·11	5·14	5·18	5·22	5·26
2	5·29	5·33	5·37	5·41	5·45	5·49	5·53	5·57	5·60	5·64
3	5·69	5·73	5·77	5·81	5·85	5·89	5·93	5·97	6·02	6·06
4	6·10	6·14	6·19	6·23	6·27	6·32	6·36	6·41	6·45	6·50
5	6·54	6·59	6·64	6·68	6·73	6·78	6·82	6·87	6·92	6·97
6	7·01	7·06	7·11	7·16	7·21	7·26	7·31	7·36	7·41	7·46
7	7·51	7·57	7·62	7·67	7·72	7·78	7·83	7·88	7·94	7·99
8	8·05	8·10	8·16	8·21	8·27	8·32	8·38	8·44	8·50	8·55
9	8·61	8·67	8·73	8·79	8·85	8·91	8·97	9·03	9·09	9·15
10	9·21	9·27	9·33	9·40	9·46	9·52	9·59	9·65	9·72	9·78
11	9·85	9·91	9·98	10·04	10·11	10·18	10·25	10·31	10·38	10·45
12	10·52	10·59	10·66	10·73	10·80	10·87	10·94	11·01	11·09	11·16
13	11·23	11·31	11·38	11·46	11·53	11·61	11·68	11·76	11·84	11·91
14	11·99	12·07	12·15	12·23	12·30	12·38	12·46	12·54	12·63	12·71
15	12·79	12·87	12·96	13·04	13·12	13·21	13·29	13·38	13·46	13·55
16	13·64	13·72	13·81	13·90	13·99	14·08	14·17	14·26	14·35	14·44
17	14·53	14·63	14·72	14·81	14·91	15·00	15·10	15·19	15·29	15·38
18	15·48	15·58	15·68	15·78	15·87	15·97	16·07	16·18	16·28	16·38
19	16·48	16·59	16·69	16·79	16·90	17·00	17·11	17·21	17·32	17·43
20	17·54	17·65	17·76	17·87	17·98	18·09	18·20	18·31	18·43	18·54
21	18·66	18·77	18·89	19·00	19·12	19·24	19·35	19·47	19·59	19·71
22	19·83	19·95	20·08	20·20	20·32	20·45	20·57	20·70	20·82	20·95
23	21·07	21·20	21·33	21·46	21·59	21·72	21·85	21·98	22·12	22·25
24	22·38	22·52	22·65	22·79	22·93	23·07	23·20	23·34	23·48	23·62
25	23·76	23·91	24·05	24·19	24·33	24·48	24·63	24·77	24·92	25·07
26	25·22	25·37	25·52	25·67	25·82	25·97	26·13	26·28	26·43	26·59
27	26·75	26·91	27·06	27·22	27·38	27·54	27·70	27·87	28·03	28·19
28	28·36	28·52	28·69	28·86	29·02	29·19	29·36	29·54	29·71	29·88
29	30·05	30·23	30·40	30·58	30·75	30·93	31·11	31·29	31·47	31·65
30	31·83	32·02	32·21	32·39	32·57	32·76	32·95	33·14	33·33	33·52
31	33·71	33·90	34·09	34·29	34·48	34·68	34·88	35·07	35·27	35·47
32	35·67	35·88	36·08	36·28	36·49	36·70	36·90	37·11	37·32	37·53
33	37·74	37·95	38·17	38·38	38·60	38·81	39·03	39·25	39·47	39·70
34	39·91	40·13	40·36	40·58	40·81	41·04	41·26	41·49	41·72	41·96

Table LXXXV.—*continued.*

Temperature.	Millimetres of Mercury.									
	0	1	2	3	4	5	6	7	8	9
35	42·19	42·42	42·66	42·89	43·13	43·37	43·61	43·85	44·09	44·33
36	44·58	44·82	45·06	45·31	45·56	45·81	46·07	46·32	46·57	46·83
37	47·08	47·34	47·60	47·86	48·12	48·38	48·64	48·91	49·17	49·44
38	49·71	49·98	50·25	50·52	50·79	51·07	51·34	51·62	51·90	52·18
39	52·46	52·74	53·03	53·31	53·60	53·88	54·17	54·46	54·75	55·05
40	55·34	55·64	55·93	56·23	56·53	56·83	57·14	57·44	57·74	58·05
41	58·36	58·67	58·98	59·29	59·61	59·92	60·24	60·56	60·88	61·20
42	61·52	61·84	62·17	62·49	62·82	63·15	63·48	63·82	64·15	64·49
43	64·82	65·16	65·50	65·84	66·19	66·53	66·88	67·23	67·58	67·93
44	68·28	68·64	68·99	69·35	69·71	70·07	70·43	70·79	71·16	71·53
45	71·90	72·27	72·64	73·01	73·39	73·76	74·14	74·52	74·90	75·29
46	75·67	76·06	76·45	76·84	77·23	77·63	78·02	78·42	78·82	79·22
47	79·62	80·03	80·43	80·84	81·25	81·66	82·07	82·49	82·91	83·32
48	83·74	84·17	84·59	85·02	85·45	85·88	86·31	86·74	87·17	87·61
49	88·05	88·49	88·93	89·38	89·82	90·27	90·72	91·18	91·63	92·09
50	92·54	93·00	93·47	93·93	94·40	94·86	95·33	95·81	96·28	96·76
51	97·24	97·72	98·20	98·68	99·17	99·66	100·2	100·6	101·1	101·6
52	102·1	102·6	103·1	103·6	104·2	104·7	105·2	105·7	106·2	106·7
53	107·2	107·8	108·3	108·8	109·3	109·9	110·4	110·9	111·5	112·0
54	112·6	113·1	113·7	114·2	114·8	115·3	115·9	116·4	117·0	117·5
55	118·1	118·7	119·2	119·8	120·4	121·0	121·6	122·1	122·7	123·3
56	124·0	124·5	125·1	125·7	126·3	126·9	127·5	128·1	128·7	129·3
57	129·9	130·5	131·1	131·8	132·4	133·0	133·6	134·3	134·9	135·5
58	136·2	136·8	137·4	138·1	138·7	139·4	140·0	140·7	141·4	142·0
59	142·7	143·4	144·0	144·7	145·4	146·0	146·7	147·4	148·1	148·8
60	149·5	150·2	150·9	151·6	152·3	153·0	153·7	154·4	155·1	155·8
61	156·5	157·2	158·0	158·7	159·4	160·1	160·9	161·6	162·4	163·1
62	163·9	164·6	165·4	166·1	166·9	167·6	168·4	169·2	169·9	170·7
63	171·5	172·3	173·0	173·8	174·6	175·4	176·2	177·0	177·8	178·6
64	179·4	180·2	181·0	181·8	182·7	183·5	184·3	185·1	186·0	186·8
65	187·6	188·5	189·3	190·2	191·0	191·9	192·7	193·6	194·5	195·5
66	196·2	197·1	197·9	198·8	199·7	200·6	201·5	202·4	203·3	204·2
67	205·1	206·0	206·9	207·8	208·7	209·6	210·6	211·5	212·4	213·4
68	214·3	215·2	216·2	217·1	218·1	219·0	220·0	221·0	221·9	222·9
69	223·9	224·8	225·8	226·8	227·8	228·8	229·8	230·8	231·8	232·8
70	233·8	234·8	235·8	236·9	237·9	238·9	239·9	241·0	242·0	243·1
71	244·1	245·2	246·2	247·3	248·4	249·4	250·5	251·6	252·6	253·7
72	254·8	255·9	257·0	258·1	259·2	260·3	261·4	262·5	263·7	264·8
73	265·9	267·0	268·2	269·3	270·5	271·6	272·8	273·9	275·1	276·2
74	277·4	278·6	279·8	280·9	282·1	283·3	284·5	285·7	286·9	288·1
75	289·3	290·5	291·8	293·0	294·2	295·4	296·7	297·9	299·2	300·4
76	301·7	302·9	304·2	305·4	306·7	308·0	309·3	310·5	311·8	313·1
77	314·4	315·7	317·0	318·3	319·7	321·0	322·3	323·6	325·0	326·3
78	327·6	329·0	330·3	331·7	333·1	334·4	335·8	337·2	338·6	339·9
79	341·3	342·7	344·1	345·5	346·9	348·3	349·8	351·2	352·6	354·0

Table LXXXV.—*continued.*

Temperature.	Millimetres of Mercury.									
	0	1	2	3	4	5	6	7	8	9
80	355·5	356·9	358·4	359·8	361·3	362·7	364·2	365·7	367·1	368·6
81	370·1	371·6	373·1	374·6	376·1	377·6	379·1	380·7	382·2	383·7
82	385·2	386·8	388·3	389·9	391·5	393·0	394·6	396·2	397·7	399·3
83	400·9	402·5	404·1	405·7	407·3	408·9	410·5	412·2	413·8	415·4
84	417·1	418·7	420·3	422·0	423·7	425·4	427·1	428·7	430·4	432·1
85	433·8	435·5	437·2	438·9	440·6	442·4	444·1	445·8	447·6	449·3
86	451·1	452·8	454·6	456·4	458·1	459·9	461·7	463·5	465·3	467·1
87	468·9	470·7	472·5	474·4	476·2	478·0	479·9	481·7	483·6	485·5
88	487·3	489·2	491·1	493·0	494·9	496·8	498·7	500·6	502·5	504·4
89	506·4	508·3	510·2	512·2	514·1	516·1	518·1	520·0	522·0	524·0
90	526·0	528·0	530·0	532·0	534·0	536·1	538·1	540·1	542·1	544·2
91	546·3	548·3	550·4	552·5	554·6	556·7	558·7	560·8	563·0	565·1
92	567·2	569·3	571·5	573·6	575·7	577·9	580·1	582·2	584·4	586·6
93	588·8	591·0	593·2	595·4	597·6	600·0	602·1	604·3	606·5	608·8
94	611·0	613·3	615·6	617·9	620·1	622·4	624·7	627·0	629·4	631·7
95	634·0	636·3	638·7	641·0	643·4	645·8	648·1	650·5	652·9	655·3
96	657·7	660·1	662·5	664·9	667·4	669·8	672·3	674·7	677·2	679·6
97	682·1	684·6	687·1	689·6	692·1	694·6	697·1	699·7	702·2	704·7
98	707·2	709·8	712·4	715·0	717·6	720·2	722·8	725·4	728·0	730·6
99	733·2	735·9	738·5	741·2	743·9	746·5	749·2	751·9	754·6	757·3
100	760·0	762·7	765·5	768·2	770·9	773·7	776·4	779·2	782·0	784·8

Table LXXXVI.—Conversion of Grms. Potassium Chloroplatinate into Grms. Potassium Chloride.

(FACTOR 0·307.)

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·000	..	..	0001	0001	0001	0002	0002	0002	0002	0003
0·001	0003	0003	0004	0004	0004	0005	0005	0005	0006	0006
0·002	0006	0006	0007	0007	0007	0008	0008	0008	0009	0009
0·003	0009	0009	0010	0010	0011	0011	0011	0012	0012	0012
0·004	0013	0013	0013	0013	0014	0014	0014	0015	0015	0015
0·005	0015	0016	0016	0016	0017	0017	0017	0017	0018	0018
0·006	0018	0019	0019	0019	0020	0020	0020	0021	0021	0021
0·007	0021	0022	0022	0022	0023	0023	0024	0024	0024	0025
0·008	0025	0025	0025	0026	0026	0026	0027	0027	0027	0028
0·009	0028	0028	0028	0029	0029	0029	0029	0030	0030	0030

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·010	0031	0031	0031	0032	0032	0032	0032	0033	0033	0033
0·011	0034	0034	0034	0035	0035	0035	0036	0036	0036	0037
0·012	0037	0037	0037	0038	0038	0038	0039	0039	0039	0040
0·013	0040	0040	0041	0041	0041	0041	0042	0042	0042	0043
0·014	0043	0043	0044	0044	0044	0045	0045	0045	0045	0046
0·015	0046	0046	0047	0047	0047	0048	0048	0048	0049	0049
0·016	0049	0049	0050	0050	0050	0051	0051	0051	0052	0052
0·017	0052	0052	0053	0053	0053	0054	0054	0054	0055	0055
0·018	0055	0056	0056	0056	0056	0057	0057	0057	0058	0058
0·019	0058	0059	0059	0059	0060	0060	0060	0060	0061	0061
0·020	0061	0061	0062	0062	0062	0063	0063	0064	0064	0064
0·021	0065	0065	0065	0065	0066	0066	0066	0067	0067	0067
0·022	0068	0068	0068	0068	0069	0069	0069	0070	0070	0070
0·023	0070	0071	0071	0072	0072	0072	0072	0073	0073	0073
0·024	0074	0074	0074	0075	0075	0075	0076	0076	0076	0076
0·025	0077	0077	0077	0078	0078	0078	0079	0079	0079	0080
0·026	0080	0080	0080	0081	0081	0081	0082	0082	0082	0083
0·027	0083	0083	0084	0084	0084	0084	0085	0085	0085	0086
0·028	0086	0086	0087	0087	0087	0087	0088	0088	0088	0089
0·029	0089	0089	0090	0090	0090	0091	0091	0091	0091	0092
0·030	0092	0092	0092	0093	0093	0094	0094	0094	0095	0095
0·031	0095	0095	0096	0096	0096	0097	0097	0097	0098	0098
0·032	0098	0099	0099	0099	0099	0100	0100	0100	0101	0101
0·033	0101	0102	0102	0102	0103	0103	0103	0103	0104	0104
0·034	0104	0105	0105	0105	0106	0106	0106	0107	0107	0107
0·035	0107	0108	0108	0108	0108	0109	0109	0109	0110	0110
0·036	0110	0111	0111	0111	0111	0112	0112	0113	0113	0113
0·037	0114	0114	0114	0115	0115	0115	0115	0116	0116	0116
0·038	0117	0117	0117	0118	0118	0118	0119	0119	0119	0119
0·039	0120	0120	0120	0121	0121	0121	0122	0122	0122	0123
0·040	0123	0123	0123	0124	0124	0124	0125	0125	0126	0126
0·041	0126	0126	0126	0127	0127	0127	0128	0128	0128	0129
0·042	0129	0129	0129	0130	0130	0130	0131	0131	0131	0132
0·043	0132	0132	0133	0133	0133	0133	0134	0134	0134	0135
0·044	0135	0135	0136	0136	0136	0137	0137	0137	0137	0138
0·045	0138	0139	0139	0139	0140	0140	0140	0140	0141	0141
0·046	0141	0141	0142	0142	0142	0143	0143	0143	0144	0144
0·047	0144	0144	0145	0145	0145	0146	0146	0146	0147	0147
0·048	0147	0148	0148	0148	0148	0149	0149	0149	0150	0150
0·049	0150	0151	0151	0151	0152	0152	0152	0152	0153	0153
0·050	0153	0154	0154	0154	0155	0155	0155	0156	0156	0156
0·051	0156	0157	0157	0157	0158	0158	0158	0159	0159	0159
0·052	0160	0160	0160	0160	0161	0161	0161	0162	0162	0162
0·053	0163	0163	0163	0164	0164	0164	0164	0165	0165	0165
0·054	0166	0166	0166	0167	0167	0167	0168	0168	0168	0168

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·055	0169	0169	0170	0170	0170	0170	0171	0171	0171	0172
0·056	0172	0172	0172	0173	0173	0173	0174	0174	0174	0175
0·057	0175	0175	0176	0176	0176	0176	0177	0177	0177	0178
0·058	0178	0178	0179	0179	0179	0179	0180	0180	0180	0181
0·059	0181	0181	0182	0182	0182	0183	0183	0183	0183	0184
0·060	0184	0184	0185	0185	0185	0186	0186	0186	0187	0187
0·061	0187	0187	0188	0188	0189	0189	0189	0190	0190	0190
0·062	0190	0191	0191	0191	0192	0192	0192	0192	0193	0193
0·063	0193	0194	0194	0194	0195	0195	0195	0195	0196	0196
0·064	0197	0197	0197	0198	0198	0198	0199	0199	0199	0199
0·065	0199	0200	0200	0200	0201	0201	0201	0202	0202	0202
0·066	0203	0203	0203	0203	0204	0204	0204	0205	0205	0205
0·067	0206	0206	0206	0207	0207	0207	0207	0208	0208	0208
0·068	0209	0209	0209	0210	0210	0210	0211	0211	0211	0211
0·069	0212	0212	0212	0213	0213	0213	0214	0214	0214	0214
0·070	0215	0215	0215	0216	0216	0217	0217	0217	0217	0218
0·071	0218	0218	0218	0219	0219	0219	0219	0220	0220	0221
0·072	0221	0221	0222	0222	0222	0222	0223	0223	0223	0224
0·073	0224	0224	0225	0225	0225	0226	0226	0226	0227	0227
0·074	0227	0227	0228	0228	0228	0229	0229	0229	0230	0230
0·075	0230	0230	0231	0231	0231	0232	0232	0232	0233	0233
0·076	0233	0234	0234	0234	0234	0235	0235	0235	0236	0236
0·077	0236	0237	0237	0237	0238	0238	0238	0238	0239	0239
0·078	0239	0240	0240	0240	0241	0241	0241	0242	0242	0242
0·079	0242	0243	0243	0243	0244	0244	0244	0245	0245	0245
0·080	0246	0246	0246	0246	0247	0247	0247	0248	0248	0248
0·081	0249	0249	0249	0249	0250	0250	0250	0251	0251	0251
0·082	0252	0252	0252	0253	0253	0253	0253	0254	0254	0254
0·083	0255	0255	0255	0256	0256	0257	0257	0257	0257	0257
0·084	0258	0258	0258	0259	0259	0259	0260	0260	0260	0261
0·085	0261	0261	0261	0262	0262	0262	0263	0263	0263	0264
0·086	0264	0264	0265	0265	0265	0265	0266	0266	0266	0267
0·087	0267	0267	0268	0268	0268	0269	0269	0269	0269	0270
0·088	0270	0270	0271	0271	0271	0272	0272	0272	0273	0273
0·089	0273	0273	0273	0274	0274	0275	0275	0275	0276	0276
0·090	0276	0277	0277	0277	0277	0278	0278	0278	0279	0279
0·091	0279	0280	0280	0280	0280	0281	0281	0281	0282	0282
0·092	0282	0283	0283	0283	0283	0284	0284	0284	0285	0285
0·093	0285	0286	0286	0286	0287	0287	0287	0288	0288	0288
0·094	0288	0289	0289	0289	0290	0290	0290	0291	0291	0291
0·095	0292	0292	0292	0292	0293	0293	0293	0294	0294	0294
0·096	0295	0295	0295	0296	0296	0296	0296	0297	0297	0297
0·097	0298	0298	0298	0299	0299	0299	0300	0300	0300	0300
0·098	0301	0301	0301	0302	0302	0302	0303	0303	0303	0304
0·099	0304	0304	0304	0305	0305	0305	0306	0306	0306	0307

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·100	0307	0307	0308	0308	0308	0309	0309	0309	0309	0309
0·101	0310	0310	0310	0311	0311	0311	0312	0312	0312	0313
0·102	0313	0313	0313	0314	0314	0314	0315	0315	0315	0316
0·103	0316	0316	0317	0317	0317	0317	0318	0318	0318	0319
0·104	0319	0319	0320	0320	0320	0321	0321	0321	0321	0322
0·105	0322	0322	0323	0323	0323	0324	0324	0324	0325	0325
0·106	0325	0325	0326	0326	0326	0327	0327	0327	0328	0328
0·107	0328	0328	0329	0329	0329	0330	0330	0330	0331	0331
0·108	0331	0332	0332	0332	0332	0333	0333	0333	0334	0334
0·109	0334	0335	0335	0335	0336	0336	0336	0337	0337	0337
0·110	0338	0338	0338	0339	0339	0339	0340	0340	0340	0340
0·111	0341	0341	0341	0342	0342	0342	0343	0343	0343	0344
0·112	0344	0344	0344	0345	0345	0345	0346	0346	0346	0347
0·113	0347	0347	0348	0348	0348	0348	0349	0349	0349	0350
0·114	0350	0350	0351	0351	0351	0352	0352	0352	0352	0353
0·115	0353	0353	0354	0354	0354	0355	0355	0355	0356	0356
0·116	0356	0356	0357	0357	0357	0358	0358	0358	0359	0359
0·117	0359	0359	0360	0360	0360	0361	0361	0361	0362	0362
0·118	0362	0363	0363	0363	0363	0364	0364	0364	0365	0365
0·119	0365	0366	0366	0366	0367	0367	0367	0367	0368	0368
0·120	0368	0369	0369	0369	0370	0370	0370	0371	0371	0371
0·121	0371	0372	0372	0372	0373	0373	0373	0374	0374	0374
0·122	0375	0375	0375	0375	0376	0376	0376	0377	0377	0377
0·123	0378	0378	0378	0379	0379	0379	0379	0380	0380	0380
0·124	0381	0381	0381	0382	0382	0382	0383	0383	0383	0383
0·125	0384	0384	0384	0385	0385	0385	0386	0386	0386	0387
0·126	0387	0387	0387	0388	0388	0388	0389	0389	0389	0390
0·127	0390	0390	0391	0391	0391	0392	0392	0392	0393	0393
0·128	0393	0393	0394	0394	0394	0394	0395	0395	0395	0396
0·129	0396	0396	0397	0397	0397	0398	0398	0398	0398	0399
0·130	0399	0399	0400	0400	0400	0401	0401	0401	0402	0402
0·131	0402	0402	0403	0403	0403	0404	0404	0404	0405	0405
0·132	0405	0406	0406	0406	0407	0407	0407	0407	0408	0408
0·133	0408	0409	0409	0409	0410	0410	0410	0410	0411	0411
0·134	0411	0412	0412	0412	0413	0413	0413	0414	0414	0414
0·135	0414	0415	0415	0415	0416	0416	0416	0417	0147	0417
0·136	0418	0418	0418	0418	0419	0419	0419	0420	0420	0420
0·137	0421	0421	0421	0422	0422	0422	0423	0423	0423	0424
0·138	0424	0424	0424	0425	0425	0425	0426	0426	0426	0426
0·139	0427	0427	0427	0428	0428	0428	0429	0429	0429	0429
0·140	0430	0430	0430	0431	0431	0431	0432	0432	0432	0433
0·141	0433	0433	0433	0434	0434	0434	0435	0435	0435	0436
0·142	0436	0436	0437	0437	0437	0437	0438	4038	0438	0439
0·143	0439	0439	0440	0440	0440	0441	0441	0441	0441	0442
0·144	0442	0442	0443	0443	0443	0444	0444	0444	0445	0445

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·145	0445	0445	0446	0446	0446	0447	0447	0447	0448	0448
0·146	0448	0449	0449	0449	0449	0450	0450	0450	0451	0451
0·147	0451	0452	0452	0452	0453	0453	0453	0453	0454	0454
0·148	0454	0455	0455	0455	0456	0456	0456	0457	0457	0457
0·149	0457	0458	0458	0458	0459	0459	0459	0460	0460	0460
0·150	0461	0461	0461	0461	0462	0462	0462	0463	0463	0463
0·151	0464	0464	0464	0464	0465	0465	0465	0466	0466	0466
0·152	0467	0467	0467	0468	0468	0468	0468	0469	0469	0469
0·153	0470	0470	0470	0471	0471	0471	0472	0472	0472	0472
0·154	0473	0473	0473	0474	0474	0474	0475	0475	0475	0476
0·155	0476	0476	0476	0477	0477	0477	0478	0478	0478	0479
0·156	0479	0479	0480	0480	0480	0480	0481	0481	0481	0482
0·157	0482	0482	0483	0483	0483	0484	0484	0484	0484	0485
0·158	0485	0485	0486	0486	0486	0487	0487	0487	0488	0488
0·159	0488	0488	0489	0489	0489	0490	0490	0490	0491	0491
0·160	0491	0492	0492	0492	0492	0493	0493	0493	0494	0494
0·161	0494	0495	0495	0495	0495	0496	0496	0496	0497	0497
0·162	0497	0498	0498	0498	0499	0499	0499	0499	0500	0500
0·163	0500	0501	0501	0501	0502	0502	0502	0503	0503	0503
0·164	0503	0504	0504	0504	0505	0505	0505	0506	0506	0506
0·165	0507	0507	0507	0507	0508	0508	0508	0509	0509	0509
0·166	0510	0510	0510	0511	0511	0511	0511	0512	0512	0512
0·167	0513	0513	0513	0514	0514	0514	0515	0515	0515	0515
0·168	0516	0516	0516	0517	0517	0517	0518	0518	0518	0519
0·169	0519	0519	0519	0520	0520	0520	0521	0521	0521	0522
0·170	0522	0522	0523	0523	0523	0523	0524	0524	0524	0525
0·171	0525	0525	0526	0526	0526	0527	0527	0527	0527	0528
0·172	0528	0528	0529	0529	0529	0530	0530	0530	0530	0531
0·173	0531	0531	0532	0532	0532	0533	0533	0533	0534	0534
0·174	0534	0534	0535	0535	0535	0536	0536	0536	0537	0537
0·175	0537	0538	0538	0538	0538	0539	0539	0539	0540	0540
0·176	0540	0541	0541	0541	0542	0542	0542	0542	0543	0543
0·177	0543	0544	0544	0544	0545	0545	0545	0546	0546	0546
0·178	0546	0547	0547	0547	0548	0548	0548	0549	0549	0549
0·179	0550	0550	0550	0550	0551	0551	0551	0552	0552	0552
0·180	0553	0553	0553	0554	0554	0554	0554	0555	0555	0555
0·181	0556	0556	0556	0557	0557	0557	0558	0558	0558	0558
0·182	0559	0559	0559	0560	0560	0560	0561	0561	0561	0562
0·183	0562	0562	0562	0563	0563	0563	0564	0564	0564	0565
0·184	0565	0565	0565	0566	0566	0566	0567	0567	0567	0568
0·185	0568	0568	0569	0569	0569	0569	0570	0570	0570	0571
0·186	0571	0571	0572	0572	0572	0573	0573	0573	0573	0574
0·187	0574	0574	0575	0575	0575	0576	0576	0576	0577	0577
0·188	0577	0577	0578	0578	0578	0579	0579	0579	0580	0580
0·189	0580	0581	0581	0581	0581	0582	0582	0582	0583	0583

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·190	0583	0584	0584	0584	0585	0585	0585	0585	0586	0586
0·191	0586	0587	0587	0587	0588	0588	0588	0589	0589	0589
0·192	0589	0590	0590	0590	0591	0591	0591	0592	0592	0592
0·193	0593	0593	0593	0593	0594	0594	0594	0595	0595	0595
0·194	0596	0596	0596	0597	0597	0597	0597	0598	0598	0598
0·195	0599	0599	0599	0600	0600	0600	0600	0601	0601	0601
0·196	0602	0602	0602	0603	0603	0603	0604	0604	0604	0604
0·197	0605	0605	0605	0606	0606	0606	0607	0607	0607	0608
0·198	0608	0608	0608	0609	0609	0609	0610	0610	0610	0611
0·199	0611	0611	0612	0612	0612	0612	0613	0613	0613	0614
0·200	0614	0614	0615	0615	0615	0616	0616	0616	0616	0617
0·201	0617	0617	0618	0618	0618	0619	0619	0619	0620	0620
0·202	0620	0620	0621	0621	0621	0622	0622	0622	0623	0623
0·203	0623	0624	0624	0624	0624	0625	0625	0625	0626	0626
0·204	0626	0627	0627	0627	0628	0628	0628	0628	0629	0629
0·205	0629	0630	0630	0630	0631	0631	0631	0631	0632	0632
0·206	0632	0633	0633	0633	0634	0634	0634	0635	0635	0635
0·207	0635	0636	0636	0636	0637	0637	0637	0638	0638	0638
0·208	0639	0639	0639	0639	0640	0640	0640	0641	0641	0641
0·209	0642	0642	0642	0643	0643	0643	0643	0644	0644	0644
0·210	0645	0645	0645	0646	0646	0646	0647	0647	0647	0647
0·211	0648	0648	0648	0649	0649	0649	0650	0650	0650	0651
0·212	0651	0651	0651	0652	0652	0652	0653	0653	0653	0654
0·213	0654	0654	0655	0655	0655	0655	0656	0656	0656	0657
0·214	0657	0657	0658	0658	0658	0659	0659	0659	0659	0660
0·215	0660	0660	0661	0661	0661	0662	0662	0662	0663	0663
0·216	0663	0663	0664	0664	0664	0665	0665	0665	0666	0666
0·217	0666	0666	0667	0667	0667	0668	0668	0668	0669	0669
0·218	0669	0670	0670	0670	0670	0671	0671	0671	0672	0672
0·219	0672	0673	0673	0673	0674	0674	0674	0674	0675	0675
0·220	0675	0676	0676	0676	0677	0677	0677	0678	0678	0678
0·221	0678	0679	0679	0679	0680	0680	0680	0681	0681	0681
0·222	0682	0682	0682	0682	0683	0683	0683	0684	0684	0684
0·223	0685	0685	0685	0686	0686	0686	0686	0687	0687	0687
0·224	0688	0688	0688	0689	0689	0689	0690	0690	0690	0690
0·225	0691	0691	0691	0692	0692	0692	0693	0693	0693	0694
0·226	0694	0694	0694	0695	0695	0695	0696	0696	0696	0697
0·227	0697	0697	0698	0698	0698	0698	0699	0699	0699	0700
0·228	0700	0700	0701	0701	0701	0701	0702	0702	0702	0703
0·229	0703	0703	0704	0704	0704	0705	0705	0705	0705	0706
0·230	0706	0706	0707	0707	0707	0708	0708	0708	0709	0709
0·231	0709	0709	0710	0710	0710	0711	0711	0711	0712	0712
0·232	0712	0713	0713	0713	0713	0714	0714	0714	0715	0715
0·233	0715	0716	0716	0716	0716	0717	0717	0717	0718	0718
0·234	0718	0719	0719	0719	0720	0720	0720	0721	0721	0721

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·235	0721	0722	0722	0722	0723	0723	0723	0724	0724	0724
0·236	0725	0725	0725	0725	0726	0726	0726	0727	0727	0727
0·237	0728	0728	0728	0729	0729	0729	0729	0730	0730	0730
0·238	0731	0731	0731	0732	0732	0732	0733	0733	0733	0733
0·239	0734	0734	0734	0735	0735	0735	0736	0736	0736	0736
0·240	0737	0737	0737	0738	0738	0738	0739	0739	0739	0740
0·241	0740	0740	0740	0741	0741	0741	0742	0742	0742	0743
0·242	0743	0743	0744	0744	0744	0744	0745	0745	0745	0746
0·243	0746	0746	0747	0747	0747	0748	0748	0478	0748	0749
0·244	0749	0749	0750	0750	0750	0751	0751	0751	0752	0752
0·245	0752	0752	0753	0753	0753	0754	0754	0754	0755	0755
0·246	0755	0756	0756	0756	0756	0757	0757	0757	0758	0758
0·247	0758	0759	0759	0759	0760	0760	0760	0760	0761	0761
0·248	0761	0762	0762	0762	0763	0763	0763	0764	0764	0764
0·249	0764	0765	0765	0765	0766	0766	0766	0767	0767	0767
0·250	0768	0768	0768	0768	0769	0769	0769	0770	0770	0770
0·251	0771	0771	0771	0771	0772	0772	0772	0773	0773	0773
0·252	0774	0774	0774	0775	0775	0775	0775	0776	0776	0776
0·253	0777	0777	0777	0778	0778	0778	0779	0779	0779	0779
0·254	0780	0780	0780	0781	0781	0781	0782	0782	0782	0783
0·255	0783	0783	0783	0784	0784	0784	0785	0785	0785	0786
0·256	0786	0786	0787	0787	0787	0787	0788	0788	0788	0789
0·257	0789	0789	0790	0790	0790	0791	0791	0791	0791	0792
0·258	0792	0792	0793	0793	0793	0794	0794	0794	0795	0795
0·259	0795	0795	0796	0796	0796	0797	0797	0797	0798	0798
0·260	0798	0799	0799	0799	0799	0800	0800	0800	0801	0801
0·261	0801	0802	0802	0802	0802	0803	0803	0803	0804	0804
0·262	0804	0805	0805	0805	0806	0806	0806	0806	0807	0807
0·263	0807	0808	0808	0808	0809	0809	0809	0810	0810	0810
0·264	0810	0811	0811	0811	0812	0812	0812	0813	0813	0813
0·265	0814	0814	0814	0814	0815	0815	0815	0816	0816	0816
0·266	0817	0817	0817	0818	0818	0818	0818	0819	0819	0819
0·267	0820	0820	0820	0821	0821	0821	0821	0822	0822	0822
0·268	0823	0823	0823	0824	0824	0824	0825	0825	0825	0825
0·269	0826	0826	0826	0827	0827	0827	0828	0828	0828	0829
0·270	0829	0829	0829	0830	0830	0830	0831	0831	0831	0831
0·271	0832	0832	0833	0833	0833	0834	0834	0834	0834	0835
0·272	0835	0835	0836	0836	0836	0837	0837	0837	0837	0838
0·273	0838	0838	0839	0839	0839	0840	0840	0840	0841	0841
0·274	0841	0841	0842	0842	0842	0843	0843	0843	0844	0844
0·275	0844	0845	0845	0845	0845	0846	0846	0846	0847	0847
0·276	0847	0848	0848	0848	0849	0849	0849	0849	0850	0850
0·277	0850	0851	0851	0851	0852	0852	0852	0853	0853	0853
0·278	0853	0854	0854	0854	0855	0855	0855	0856	0856	0856
0·279	0857	0857	0857	0857	0858	0858	0858	0859	0859	0859

Table LXXXVI.—K_2PtCl_6 to KCl.—*continued.*

K_2PtCl_6. Grm.	Grm. KCl.									
	0	1	2	3	4	5	6	7	8	9
0·280	0860	0860	0860	0861	0861	0861	0861	0862	0862	0862
0·281	0863	0863	0863	0864	0864	0864	0865	0865	0865	0865
0·282	0866	0866	0866	0867	0867	0867	0868	0868	0868	0869
0·283	0869	0869	0869	0870	0870	0870	0871	0871	0871	0872
0·284	0872	0872	0872	0873	0873	0873	0874	0874	0874	0875
0·285	0875	0875	0876	0876	0876	0876	0877	0877	0877	0878
0·286	0878	0878	0879	0879	0879	0880	0880	0880	0880	0881
0·287	0881	0881	0882	0882	0882	0883	0883	0883	0884	0884
0·288	0884	0884	0885	0885	0885	0886	0886	0886	0887	0887
0·289	0887	0888	0888	0888	0888	0889	0889	0889	0890	0890
0·290	0890	0891	0891	0891	0892	0892	0892	0892	0893	0893
0·291	0893	0894	0894	0894	0895	0895	0895	0896	0896	0896
0·292	0896	0897	0897	0897	0898	0898	0898	0899	0899	0899
0·293	0900	0900	0900	0900	0901	0901	0901	0902	0902	0902
0·294	0903	0903	0903	0904	0904	0904	0904	0905	0905	0905
0·295	0906	0906	0906	0907	0907	0907	0907	0908	0908	0908
0·296	0909	0909	0909	0910	0910	0910	0911	0911	0911	0911
0·297	0912	0912	0912	0913	0913	0913	0914	0914	0914	0915
0·298	0915	0915	0915	0916	0916	0916	0917	0917	0917	0918
0·299	0918	0918	0919	0919	0919	0919	0920	0920	0920	0921
0·300	0921	0921	0922	0922	0922	0923	0923	0923	0923	0924
0·301	0924	0924	0925	0925	0925	0926	0926	0926	0927	0927
0·302	0927	0927	0928	0928	0928	0929	0929	0929	0930	0930
0·303	0930	0931	0931	0931	0931	0932	0932	0932	0933	0933
0·304	0933	0934	0934	0934	0935	0935	0935	0935	0936	0936
0·305	0936	0937	0937	0937	0938	0938	0938	0938	0939	0939
0·306	0939	0940	0940	0940	0941	0941	0941	0942	0942	0942
0·307	0942	0943	0943	0943	0944	0944	0944	0945	0945	0945
0·308	0946	0946	0946	0946	0947	0947	0947	0948	0948	0948
0·309	0949	0949	0949	0950	0950	0950	0950	0951	0951	0951
0·310	0952	0952	0952	0953	0953	0953	0954	0954	0954	0955
0·311	0955	0955	0955	0956	0956	0956	0957	0957	0957	0958
0·312	0958	0958	0959	0959	0959	0959	0960	0960	0960	0961
0·313	0961	0961	0962	0962	0962	0963	0963	0963	0964	0964
0·314	0964	0965	0965	0965	0966	0966	0966	0966	0967	0967
0·315	0967	0968	0968	0968	0969	0969	0969	0969	0970	0970
0·316	0970	0970	0971	0971	0971	0972	0972	0972	0973	0973
0·317	0973	0973	0974	0974	0974	0975	0975	0975	0976	0976
0·318	0976	0977	0977	0977	0977	0978	0978	0978	0979	0979
0·319	0979	0980	0980	0980	0981	0981	0981	0981	0982	0982
0·320	0982	0983	0983	0983	0984	0984	0984	0985	0985	0985
0·321	0985	0986	0986	0986	0987	0987	0987	0988	0988	0988
0·322	0989	0989	0989	0989	0990	0990	0990	0991	0991	0991
0·323	0992	0992	0992	0993	0993	0993	0993	0994	0994	0994
0·324	0994	0995	0995	0996	0996	0996	0997	0997	0997	0997
0·325	0998	0998	0998	0999	0999	0999	1000	1000	1000	1001

Table LXXXVII.—Conversion of Grms. of Potassium Perchlorate ($KClO_4$) into Grms. Potassium Chloride (KCl).

(Factor 0·538.)

$KClO_4$. Grm.	0	1	2	3	4	5	6	7	8	9
0·000	..	0001	0001	0002	0002	0003	0003	0004	0004	0005
0·001	0005	0006	0006	0007	0008	0008	0009	0009	0010	0010
0·002	0011	0011	0012	0012	0013	0013	0014	0015	0015	0016
0·003	0016	0017	0017	0018	0018	0019	0019	0020	0020	0021
0·004	0022	0022	0023	0023	0024	0024	0025	0025	0026	0026
0·005	0027	0027	0028	0029	0029	0030	0030	0031	0031	0032
0·006	0032	0033	0033	0034	0034	0035	0036	0036	0037	0037
0·007	0038	0038	0039	0039	0040	0040	0041	0041	0042	0043
0·008	0043	0044	0044	0045	0045	0046	0046	0047	0047	0048
0·009	0048	0049	0049	0050	0051	0051	0052	0052	0053	0053
0·010	0054	0054	0055	0055	0056	0056	0057	0058	0058	0059
0·011	0059	0060	0060	0061	0061	0062	0062	0063	0063	0064
0·012	0065	0065	0066	0066	0067	0067	0068	0068	0069	0069
0·013	0070	0070	0071	0072	0072	0073	0073	0074	0074	0075
0·014	0075	0076	0076	0077	0077	0078	0079	0079	0080	0080
0·015	0081	0081	0082	0082	0083	0083	0084	0084	0085	0086
0·016	0086	0087	0087	0088	0088	0089	0089	0090	0090	0091
0·017	0091	0092	0093	0093	0094	0094	0095	0095	0096	0096
0·018	0097	0097	0098	0098	0099	0100	0100	0101	0101	0102
0·019	0102	0103	0103	0104	0104	0105	0105	0106	0107	0107
0·020	0108	0108	0109	0109	0110	0110	0111	0111	0112	0112
0·021	0113	0114	0114	0115	0115	0116	0116	0117	0117	0118
0·022	0118	0119	0119	0120	0121	0121	0122	0122	0123	0123
0·023	0124	0124	0125	0125	0126	0126	0127	0128	0128	0129
0·024	0129	0130	0130	0131	0131	0132	0132	0133	0133	0134
0·025	0135	0135	0136	0136	0137	0137	0138	0138	0139	0139
0·026	0140	0140	0141	0141	0142	0143	0143	0144	0144	0145
0·027	0145	0146	0146	0147	0147	0148	0148	0149	0150	0150
0·028	0151	0151	0152	0152	0153	0153	0154	0154	0155	0155
0·029	0156	0157	0157	0158	0158	0159	0159	0160	0160	0161
0·030	0161	0162	0162	0163	0164	0164	0165	0165	0166	0166
0·031	0167	0167	0168	0168	0169	0169	0170	0170	0171	0172
0·032	0172	0173	0173	0174	0174	0175	0175	0176	0176	0177
0·033	0178	0178	0179	0179	0180	0180	0181	0181	0182	0182
0·034	0183	0183	0184	0184	0185	0186	0186	0187	0187	0188
0·035	0188	0189	0189	0190	0190	0191	0192	0192	0193	0193
0·036	0194	0194	0195	0195	0196	0196	0197	0197	0198	0199
0·037	0199	0200	0200	0201	0201	0202	0202	0203	0203	0204
0·038	0204	0205	0206	0206	0207	0207	0208	0208	0209	0209
0·039	0210	0210	0211	0211	0212	0213	0213	0214	0214	0215
0·040	0215	0216	0216	0217	0217	0218	0218	0219	0220	0220
0·041	0221	0221	0222	0222	0223	0223	0224	0224	0225	0225
0·042	0226	0226	0227	0228	0228	0229	0229	0230	0230	0231
0·043	0231	0232	0232	0233	0233	0234	0235	0235	0236	0236
0·044	0237	0237	0238	0238	0239	0239	0240	0240	0241	0242

Table LXXXVII.—$KClO_4$ to KCl.—*continued.*

$KClO_4$. Grm.	0	1	2	3	4	5	6	7	8	9
0·045	0242	0243	0243	0244	0244	0245	0245	0246	0246	0247
0·046	0247	0248	0249	0249	0250	0250	0251	0251	0252	0252
0·047	0253	0253	0254	0254	0255	0256	0256	0257	0257	0258
0·048	0258	0259	0259	0260	0260	0261	0261	0262	0263	0263
0·049	0264	0264	0265	0265	0266	0266	0267	0267	0268	0268
0·050	0269	0270	0270	0271	0271	0272	0272	0273	0273	0274
0·051	0274	0275	0275	0276	0277	0277	0278	0278	0279	0279
0·052	0280	0280	0281	0281	0282	0282	0283	0284	0284	0285
0·053	0285	0286	0286	0287	0287	0288	0288	0289	0289	0290
0·054	0291	0291	0292	0292	0293	0293	0294	0294	0295	0295
0·055	0296	0296	0297	0298	0298	0299	0299	0300	0300	0301
0·056	0301	0302	0302	0303	0303	0304	0305	0305	0306	0306
0·057	0307	0307	0308	0308	0309	0309	0310	0310	0311	0312
0·058	0312	0313	0313	0314	0314	0315	0315	0316	0316	0317
0·059	0317	0318	0318	0319	0320	0320	0321	0321	0322	0322
0·060	0323	0323	0324	0324	0325	0325	0326	0327	0327	0328
0·061	0328	0329	0329	0330	0330	0331	0331	0332	0332	0333
0·062	0334	0334	0335	0335	0336	0336	0337	0337	0338	0338
0·063	0339	0339	0340	0341	0341	0342	0342	0343	0343	0344
0·064	0344	0345	0345	0346	0346	0347	0348	0348	0349	0349
0·065	0350	0350	0351	0351	0351	0352	0352	0353	0354	0355
0·066	0355	0356	0356	0357	0357	0358	0359	0359	0359	0360
0·067	0360	0361	0362	0363	0363	0363	0364	0364	0365	0365
0·068	0366	0366	0367	0367	0368	0369	0369	0370	0370	0371
0·069	0371	0372	0372	0373	0373	0374	0374	0375	0376	0376
0·070	0377	0377	0378	0378	0379	0379	0380	0380	0381	0381
0·071	0382	0383	0383	0384	0384	0385	0385	0386	0386	0387
0·072	0387	0388	0388	0389	0390	0390	0391	0391	0392	0392
0·073	0393	0393	0394	0394	0395	0395	0396	0397	0397	0398
0·074	0398	0399	0399	0400	0400	0401	0401	0402	0402	0403
0·075	0404	0404	0405	0405	0406	0406	0407	0407	0408	0408
0·076	0409	0409	0410	0410	0411	0412	0412	0413	0413	0414
0·077	0414	0415	0415	0416	0416	0417	0417	0418	0419	0419
0·078	0420	0420	0421	0421	0422	0422	0423	0423	0424	0425
0·079	0425	0426	0426	0427	0427	0428	0429	0429	0430	0430
0·080	0430	0431	0431	0432	0433	0433	0434	0434	0435	0435
0·081	0436	0436	0437	0437	0438	0438	0439	0440	0440	0441
0·082	0441	0442	0442	0443	0443	0444	0445	0445	0445	0446
0·083	0447	0447	0448	0448	0449	0449	0450	0450	0451	0451
0·084	0452	0452	0453	0454	0454	0455	0455	0456	0456	0457
0·085	0457	0458	0458	0459	0459	0460	0461	0461	0462	0462
0·086	0463	0463	0464	0464	0465	0465	0466	0467	0467	0468
0·087	0468	0469	0469	0470	0470	0471	0471	0472	0472	0473
0·088	0473	0474	0475	0475	0476	0476	0477	0477	0478	0478
0·089	0479	0479	0480	0480	0481	0482	0482	0483	0483	0484
0·090	0484	0485	0485	0486	0486	0487	0487	0488	0489	0489
0·091	0490	0490	0491	0491	0492	0492	0493	0493	0494	0494
0·092	0495	0495	0496	0497	0497	0498	0498	0499	0499	0500
0·093	0500	0501	0501	0502	0503	0504	0504	0504	0505	0505
0·094	0506	0506	0507	0507	0508	0508	0509	0509	0510	0511

Table LXXXVII.—KClO$_4$ to KCl.—*continued.*

KClO$_4$. Grm.	0	1	2	3	4	5	6	7	8	9
0·095	0511	0512	0512	0513	0513	0514	0514	0515	0515	0516
0·096	0516	0517	0518	0518	0519	0519	0520	0520	0521	0521
0·097	0522	0522	0523	0523	0523	0524	0525	0526	0526	0527
0·098	0527	0528	0528	0529	0529	0530	0530	0531	0532	0532
0·099	0533	0533	0534	0534	0535	0535	0536	0536	0537	0537
0·100	0538	0539	0539	0540	0540	0541	0541	0542	0542	0543
0·101	0543	0544	0544	0545	0546	0546	0547	0547	0548	0548
0·102	0549	0549	0550	0550	0551	0551	0552	0553	0553	0554
0·103	0554	0555	0555	0556	0556	0557	0557	0558	0559	0559
0·104	0560	0560	0561	0561	0562	0562	0563	0563	0564	0564
0·105	0565	0566	0566	0567	0567	0568	0568	0569	0569	0570
0·106	0570	0571	0571	0572	0573	0573	0574	0574	0575	0575
0·107	0576	0576	0577	0577	0578	0578	0579	0580	0580	0581
0·108	0581	0582	0582	0583	0583	0584	0584	0585	0585	0586
0·109	0587	0587	0588	0588	0589	0589	0590	0590	0591	0591
0·110	0592	0592	0593	0594	0594	0595	0595	0596	0596	0597
0·111	0597	0598	0598	0599	0599	0600	0601	0602	0602	0603
0·112	0603	0603	0604	0604	0605	0605	0606	0606	0607	0608
0·113	0608	0608	0609	0610	0610	0611	0611	0612	0612	0613
0·114	0613	0614	0614	0615	0616	0616	0617	0617	0618	0618
0·115	0619	0619	0620	0620	0621	0621	0622	0623	0623	0624
0·116	0624	0625	0625	0626	0626	0627	0627	0628	0629	0629
0·117	0629	0630	0631	0631	0632	0632	0633	0633	0634	0634
0·118	0635	0635	0636	0636	0637	0638	0638	0639	0639	0640
0·119	0640	0641	0641	0642	0642	0643	0643	0644	0645	0645
0·120	0646	0646	0647	0647	0648	0648	0649	0649	0650	0650
0·121	0651	0652	0652	0653	0653	0654	0654	0655	0655	0656
0·122	0656	0657	0657	0658	0659	0660	0660	0661	0661	0662
0·123	0662	0663	0663	0664	0664	0665	0665	0666	0666	0667
0·124	0667	0668	0668	0669	0669	0670	0670	0671	0671	0672
0·125	0673	0673	0674	0674	0675	0675	0676	0676	0677	0677
0·126	0678	0678	0679	0680	0680	0681	0681	0682	0682	0683
0·127	0683	0684	0684	0685	0685	0686	0687	0687	0688	0688
0·128	0689	0689	0690	0690	0691	0691	0692	0692	0693	0694
0·129	0694	0695	0695	0696	0696	0697	0697	0698	0698	0699
0·130	0699	0700	0700	0701	0701	0702	0702	0703	0703	0704
0·131	0704	0705	0705	0706	0706	0707	0707	0708	0709	0709
0·132	0710	0710	0711	0711	0712	0712	0713	0714	0714	0715
0·133	0715	0716	0716	0717	0717	0718	0718	0719	0719	0720
0·134	0721	0721	0722	0722	0723	0723	0724	0724	0725	0725
0 135	0726	0726	0727	0727	0728	0729	0729	0730	0730	0731
0·136	0731	0732	0732	0733	0733	0734	0734	0735	0736	0736
0·137	0737	0738	0738	0739	0739	0740	0740	0741	0741	0742
0·138	0742	0743	0744	0744	0745	0745	0746	0746	0747	0747
0·139	0748	0748	0749	0749	0750	0751	0751	0752	0752	0753
0·140	0753	0754	0754	0755	0755	0756	0756	0757	0758	0758
0·141	0759	0759	0760	0760	0761	0761	0762	0762	0763	0763
0·142	0764	0765	0765	0766	0766	0767	0767	0768	0768	0769
0·143	0769	0770	0770	0771	0771	0772	0773	0773	0774	0774
0·144	0775	0775	0776	0776	0777	0777	0778	0779	0779	0780

Table LXXXVII.—$KClO_4$ to KCl.—*continued.*

$KClO_4$. Grm.	0	1	2	3	4	5	6	7	8	9
0·145	0780	0781	0781	0782	0782	0783	0783	0784	0784	0785
0·146	0785	0786	0787	0787	0788	0788	0789	0789	0790	0790
0·147	0791	0791	0792	0793	0793	0794	0794	0795	0795	0796
0·148	0796	0797	0797	0798	0798	0799	0800	0800	0801	0801
0·149	0802	0802	0803	0803	0804	0804	0805	0805	0806	0807
0·150	0807	0808	0808	0809	0809	0810	0810	0811	0811	0811
0·151	0812	0812	0813	0813	0814	0814	0815	0815	0816	0817
0·152	0817	0818	0818	0819	0819	0820	0820	0821	0821	0822
0·153	0823	0823	0824	0825	0825	0826	0826	0827	0827	0828
0·154	0829	0829	0830	0830	0831	0831	0832	0832	0833	0833
0·155	0834	0834	0835	0836	0836	0837	0837	0838	0838	0839
0·156	0839	0840	0840	0841	0841	0842	0843	0843	0844	0844
0·157	0845	0845	0846	0846	0847	0847	0848	0848	0849	0850
0·158	0850	0851	0851	0852	0852	0853	0853	0854	0854	0855
0·159	0855	0856	0856	0857	0858	0859	0859	0860	0860	0861
0·160	0861	0862	0862	0863	0863	0864	0864	0865	0866	0866
0·161	0867	0867	0868	0868	0869	0869	0870	0870	0871	0871
0·162	0872	0873	0873	0874	0874	0875	0875	0876	0876	0877
0·163	0877	0878	0878	0879	0879	0880	0880	0881	0881	0882
0·164	0882	0883	0883	0884	0884	0885	0886	0886	0887	0887
0·165	0888	0888	0889	0890	0890	0891	0891	0892	0892	0893
0·166	0893	0894	0894	0895	0895	0896	0896	0897	0897	0898
0·167	0898	0899	0900	0900	0901	0901	0902	0902	0903	0903
0·168	0904	0904	0905	0905	0906	0907	0907	0908	0908	0909
0·169	0909	0910	0910	0911	0911	0912	0912	0913	0914	0914
0·170	0915	0915	0916	0916	0917	0917	0918	0918	0919	0919
0·171	0920	0921	0921	0922	0922	0923	0923	0924	0924	0925
0·172	0925	0926	0926	0927	0928	0928	0929	0929	0930	0930
0·173	0931	0931	0932	0932	0933	0933	0934	0935	0935	0936
0·174	0936	0937	0937	0938	0938	0939	0939	0940	0940	0941
0·175	0942	0942	0943	0943	0944	0944	0945	0945	0946	0946
0·176	0947	0947	0948	0948	0949	0949	0950	0950	0951	0952
0·177	0952	0953	0953	0954	0954	0955	0955	0956	0957	0957
0·178	0958	0959	0959	0960	0960	0961	0961	0962	0962	0962
0·179	0963	0963	0964	0964	0965	0966	0966	0967	0967	0968
0·180	0968	0969	0969	0970	0971	0971	0972	0972	0973	0973
0·181	0974	0974	0975	0975	0976	0976	0977	0978	0978	0979
0·182	0979	0980	0980	0981	0981	0982	0982	0983	0983	0984
0·183	0985	0985	0986	0986	0987	0987	0988	0988	0989	0989
0·184	0990	0990	0991	0992	0992	0993	0993	0994	0994	0995
0·185	0995	0996	0996	0997	0997	0998	0999	0999	1000	1000
0·186	1001	1001	1002	1002	1003	1003	1004	1004	1004	1005
0·187	1006	1006	1007	1007	1008	1008	1009	1009	1010	1010
0·188	1011	1011	1012	1013	1013	1014	1014	1015	1015	1016
0·189	1017	1017	1018	1018	1019	1019	1020	1021	1021	1022
0·190	1022	1023	1023	1024	1024	1025	1025	1026	1027	1027
0·191	1028	1028	1029	1029	1030	1030	1031	1031	1032	1032
0·192	1033	1033	1034	1035	1035	1036	1036	1037	1037	1038
0·193	1038	1039	1039	1040	1040	1041	1042	1042	1043	1043
0·194	1044	1044	1045	1045	1046	1046	1047	1047	1048	1049
0·195	1049	1050	1050	1051	1051	1052	1052	1053	1053	1054
0·196	1054	1055	1056	1056	1057	1057	1058	1058	1059	1059
0·197	1060	1060	1061	1061	1062	1062	1063	1064	1064	1065
0·198	1065	1066	1066	1067	1067	1068	1068	1069	1070	1070
0·199	1071	1071	1072	1072	1073	1073	1073	1074	1074	1075

Table LXXXVIII.—Conversion of Grms. of Potassium Chloride (KCl) into Grms. of Potassium Oxide (K_2O).

(FACTOR 0·632.)

KCl. Grm.	Grm. K_2O.									
	0	1	2	3	4	5	6	7	8	9
0·000	..	0001	0001	0002	0003	0003	0004	0005	0005	0006
0·001	0006	0007	0008	0008	0009	0009	0010	0011	0011	0012
0·002	0013	0013	0014	0015	0015	0016	0016	0017	0018	0018
0·003	0019	0020	0020	0021	0021	0022	0023	0023	0024	0025
0·004	0025	0026	0027	0027	0028	0028	0029	0030	0030	0031
0·005	0032	0032	0033	0033	0034	0035	0035	0036	0037	0037
0·006	0038	0039	0039	0040	0040	0041	0042	0042	0043	0044
0·007	0044	0045	0046	0046	0047	0047	0048	0049	0050	0050
0·008	0051	0051	0052	0052	0053	0054	0054	0055	0056	0056
0·009	0057	0058	0058	0059	0059	0060	0060	0061	0062	0063
0·010	0063	0064	0064	0065	0066	0066	0067	0068	0069	0070
0·011	0070	0070	0071	0071	0072	0073	0073	0074	0075	0075
0·012	0076	0077	0077	0078	0078	0079	0080	0080	0081	0082
0·013	0082	0083	0083	0084	0085	0085	0086	0087	0087	0088
0·014	0088	0089	0090	0091	0091	0092	0092	0093	0094	0094
0·015	0095	0095	0096	0097	0097	0098	0099	0099	0100	0100
0·016	0101	0102	0102	0103	0104	0104	0105	0106	0106	0107
0·017	0107	0108	0109	0109	0110	0111	0111	0112	0112	0113
0·018	0114	0114	0115	0116	0116	0117	0118	0118	0119	0119
0·019	0120	0121	0121	0122	0123	0123	0124	0125	0125	0126
0·020	0126	0127	0128	0128	0129	0130	0130	0131	0131	0132
0·021	0133	0133	0134	0135	0135	0136	0137	0137	0138	0138
0·022	0139	0140	0140	0141	0142	0142	0143	0143	0144	0145
0·023	0145	0146	0147	0147	0148	0149	0150	0150	0151	0152
0·024	0152	0153	0154	0154	0155	0155	0156	0157	0157	0158
0·025	0158	0159	0159	0160	0161	0161	0162	0162	0163	0164
0·026	0165	0166	0166	0167	0167	0168	0169	0169	0170	0171
0·027	0171	0171	0172	0173	0173	0174	0174	0175	0176	0176
0·028	0177	0178	0178	0179	0179	0180	0181	0181	0182	0183
0·029	0183	0184	0185	0185	0186	0186	0187	0188	0189	0189
0·030	0190	0190	0191	0191	0192	0193	0193	0194	0195	0195
0·031	0196	0197	0197	0198	0198	0199	0200	0200	0201	0202
0·032	0202	0203	0204	0204	0205	0205	0206	0207	0207	0208
0·033	0209	0209	0210	0210	0211	0212	0212	0213	0214	0214
0·034	0215	0216	0216	0217	0217	0218	0219	0219	0220	0221
0·035	0221	0222	0222	0223	0224	0224	0225	0226	0226	0227
0·036	0228	0228	0229	0229	0230	0231	0231	0232	0233	0233
0·037	0234	0234	0235	0236	0236	0237	0238	0238	0239	0240
0·038	0240	0241	0241	0242	0243	0243	0244	0245	0245	0246
0·039	0246	0247	0248	0248	0249	0250	0250	0251	0252	0252

Table LXXXVIII.—KCl to K_2O.—*continued.*

KCl. Grm.	Grm. K_2O.									
	0	1	2	3	4	5	6	7	8	9
0·040	0253	0253	0254	0255	0255	0256	0257	0257	0258	0258
0·041	0259	0260	0260	0261	0262	0262	0263	0264	0264	0265
0·042	0265	0266	0267	0267	0268	0269	0269	0270	0270	0271
0·043	0272	0272	0273	0274	0274	0275	0276	0276	0277	0277
0·044	0278	0279	0279	0280	0281	0281	0282	0282	0283	0284
0·045	0284	0285	0286	0286	0287	0287	0288	0289	0289	0290
0·046	0291	0291	0292	0293	0293	0294	0294	0295	0296	0296
0·047	0297	0298	0298	0299	0299	0300	0301	0301	0302	0303
0·048	0303	0304	0305	0305	0306	0306	0307	0308	0308	0309
0·049	0310	0310	0311	0311	0312	0313	0313	0314	0315	0315
0·050	0316	0317	0317	0318	0318	0319	0320	0320	0321	0322
0·051	0322	0323	0323	0324	0325	0325	0326	0327	0327	0328
0·052	0329	0329	0330	0330	0331	0332	0332	0333	0334	0334
0·053	0335	0335	0336	0337	0337	0338	0339	0339	0340	0341
0·054	0341	0342	0342	0343	0344	0344	0345	0346	0346	0347
0·055	0348	0348	0349	0349	0350	0351	0351	0352	0353	0353
0·056	0354	0355	0355	0356	0356	0357	0358	0358	0359	0360
0·057	0360	0361	0361	0362	0363	0363	0364	0365	0365	0366
0·058	0366	0367	0368	0368	0369	0370	0370	0371	0372	0372
0·059	0373	0373	0374	0375	0375	0376	0377	0377	0378	0378
0·060	0379	0380	0380	0381	0382	0382	0383	0384	0384	0385
0·061	0385	0386	0387	0387	0388	0389	0389	0390	0390	0391
0·062	0392	0392	0393	0394	0394	0395	0396	0396	0397	0397
0·063	0398	0399	0399	0400	0401	0401	0402	0403	0403	0404
0·064	0404	0405	0406	0406	0407	0408	0408	0409	0409	0410
0·065	0411	0411	0412	0413	0413	0414	0414	0415	0416	0416
0·066	0417	0418	0418	0419	0420	0420	0421	0421	0422	0423
0·067	0423	0424	0425	0425	0426	0427	0247	0428	0428	0429
0·068	0430	0430	0431	0432	0432	0433	0433	0434	0435	0435
0·069	0436	0437	0437	0438	0439	0439	0440	0440	0441	0442
0·070	0442	0443	0444	0444	0445	0445	0446	0447	0447	0448
0·071	0449	0449	0450	0451	0451	0452	0452	0453	0454	0454
0·072	0455	0456	0456	0457	0457	0458	0459	0459	0460	0461
0·073	0461	0462	0463	0463	0464	0464	0465	0466	0466	0467
0·074	0468	0468	0469	0469	0470	0471	0471	0472	0473	0473
0·075	0474	0475	0475	0476	0476	0477	0478	0478	0479	0480
0·076	0480	0481	0481	0482	0483	0483	0484	0485	0485	0486
0·077	0487	0487	0488	0488	0489	0490	0490	0491	0492	0492
0·078	0493	0493	0494	0495	0495	0496	0497	0497	0498	0499
0·079	0499	0500	0500	0501	0502	0502	0503	0504	0504	0505
0·080	0506	0506	0507	0507	0508	0509	0509	0510	0511	0511
0·081	0512	0512	0513	0514	0514	0515	0516	0516	0517	0518
0·082	0518	0519	0519	0520	0521	0521	0522	0523	0523	0524
0·083	0524	0525	0526	0526	0527	0528	0528	0529	0530	0530
0·084	0531	0531	0532	0533	0533	0534	0535	0535	0536	0536

Table LXXXVIII.—KCl to K_2O.—*continued.*

KCl. Grm.	Grm. K_2O.									
	0	1	2	3	4	5	6	7	8	9
0·085	0537	0538	0538	0539	0540	0540	0541	0542	0542	0543
0·086	0543	0544	0545	0545	0546	0547	0547	0548	0548	0549
0·087	0550	0550	0551	0552	0552	0553	0554	0554	0555	0555
0·088	0556	0557	0557	0558	0559	0559	0560	0560	0561	0562
0·089	0562	0563	0564	0564	0565	0566	0566	0567	0567	0568
0·090	0569	0569	0570	0571	0571	0572	0572	0573	0574	0574
0·091	0575	0576	0576	0577	0578	0578	0579	0579	0580	0581
0·092	0581	0582	0583	0583	0584	0585	0585	0586	0586	0587
0·093	0588	0588	0589	0590	0590	0591	0591	0592	0593	0593
0·094	0594	0595	0595	0596	0597	0597	0598	0598	0599	0600
0·095	0600	0601	0602	0602	0603	0603	0604	0605	0605	0606
0·096	0607	0607	0608	0609	0610	0610	0610	0611	0612	0612
0·097	0613	0614	0615	0615	0616	0617	0617	0618	0619	0619
0·098	0619	0620	0621	0621	0622	0622	0623	0624	0624	0625
0·099	0626	0626	0627	0627	0628	0629	0629	0630	0631	0631
0·100	0632	0633	0633	0634	0634	0635	0635	0636	0637	0637
0·101	0638	0638	0639	0639	0640	0641	0642	0643	0643	0644
0·102	0645	0645	0646	0647	0647	0648	0648	0649	0650	0650
0·103	0651	0652	0652	0653	0653	0654	0654	0655	0656	0657
0·104	0657	0658	0659	0659	0660	0660	0661	0662	0662	0663
0·105	0664	0664	0665	0666	0666	0667	0668	0669	0669	0670
0·106	0670	0671	0671	0672	0672	0673	0673	0674	0675	0676
0·107	0676	0677	0678	0678	0679	0679	0680	0681	0681	0682
0·108	0683	0683	0684	0684	0685	0686	0686	0687	0688	0688
0·109	0689	0690	0690	0691	0691	0692	0693	0693	0694	0695
0·110	0695	0696	0696	0697	0698	0698	0699	0700	0700	0701
0·111	0702	0702	0703	0703	0704	0705	0705	0706	0707	0707
0·112	0708	0708	0709	0710	0710	0711	0712	0712	0713	0714
0·113	0714	0715	0715	0716	0717	0717	0718	0718	0719	0719
0·114	0720	0721	0722	0722	0723	0724	0724	0725	0726	0726
0·115	0727	0727	0728	0729	0729	0730	0731	0731	0732	0732
0·116	0733	0734	0734	0735	0736	0736	0737	0738	0738	0739
0·117	0739	0740	0741	0741	0742	0743	0743	0744	0744	0745
0·118	0746	0746	0747	0748	0748	0749	0750	0750	0751	0751
0·119	0752	0753	0753	0754	0755	0755	0756	0757	0758	0758
0·120	0758	0759	0760	0760	0761	0762	0762	0763	0763	0764
0·121	0765	0765	0766	0767	0767	0768	0769	0769	0770	0770
0·122	0771	0772	0772	0773	0774	0774	0775	0775	0776	0777
0·123	0778	0779	0779	0780	0781	0781	0782	0782	0783	0784
0·124	0784	0785	0786	0786	0787	0788	0788	0789	0790	0790
0·125	0791	0791	0792	0792	0793	0793	0794	0794	0795	0795
0·126	0796	0797	0797	0798	0799	0799	0800	0800	0801	0802
0·127	0802	0803	0803	0804	0805	0805	0806	0807	0807	0808
0·128	0809	0809	0810	0811	0811	0812	0812	0813	0814	0814
0·129	0815	0816	0816	0817	0817	0818	0819	0819	0820	0821

Table LXXXVIII.—KCl to K_2O.—*continued.*

KCl. Grm.	Grm. K_2O.									
	0	1	2	3	4	5	6	7	8	9
0·130	0821	0822	0822	0823	0824	0824	0825	0826	0826	0827
0·131	0827	0828	0829	0829	0830	0831	0831	0832	0833	0833
0·132	0834	0835	0835	0836	0836	0837	0838	0838	0839	0840
0·133	0840	0841	0842	0843	0843	0844	0844	0845	0846	0846
0·134	0847	0847	0848	0848	0849	0850	0850	0851	0852	0852
0·135	0853	0854	0854	0855	0856	0856	0857	0858	0858	0859
0·136	0860	0861	0862	0862	0863	0864	0864	0865	0865	0866
0·137	0866	0867	0867	0868	0868	0869	0869	0870	0871	0871
0·138	0872	0873	0873	0874	0874	0875	0876	0876	0877	0878
0·139	0878	0879	0880	0880	0881	0881	0882	0883	0883	0884
0·140	0885	0885	0886	0887	0887	0888	0889	0889	0890	0890
0·141	0891	0892	0892	0893	0894	0894	0895	0896	0896	0897
0·142	0897	0898	0899	0899	0900	0901	0901	0902	0902	0903
0·143	0904	0904	0905	0906	0906	0907	0908	0908	0909	0909
0·144	0910	0910	0911	0912	0912	0913	0914	0914	0915	0915
0·145	0916	0917	0918	0918	0919	0920	0920	0921	0921	0922
0·146	0923	0923	0924	0925	0925	0926	0927	0927	0928	0928
0·147	0929	0930	0930	0931	0932	0932	0933	0933	0934	0935
0·148	0935	0936	0937	0937	0938	0939	0939	0940	0940	0941
0·149	0942	0942	0943	0944	0944	0945	0945	0946	0947	0947
0·150	0948	0949	0949	0950	0951	0951	0952	0952	0953	0954
0·151	0954	0955	0956	0956	0957	0957	0958	0959	0959	0960
0·152	0961	0961	0962	0963	0963	0964	0964	0965	0966	0966
0·153	0967	0968	0968	0969	0969	0970	0971	0971	0972	0973
0·154	0973	0974	0975	0975	0976	0976	0977	0978	0978	0979
0·155	0980	0980	0981	0981	0982	0983	0983	0984	0985	0985
0·156	0986	0987	0987	0988	0988	0989	0990	0991	0991	0992
0·157	0992	0993	0994	0994	0995	0995	0996	0997	0997	0998
0·158	0999	0999	1000	1000	1001	1002	1002	1003	1004	1004
0·159	1005	1006	1006	1007	1007	1008	1009	1009	1010	1011
0·160	1011	1012	1012	1013	1014	1014	1015	1016	1016	1017

Table LXXXIX.—Conversion of Grms. of Sodium Chloride (NaCl) into Grms. of Sodium Oxide (Na_2O).

(FACTOR 0·530.)

Grm. NaCl.	Grm. Na_2O.									
	0	1	2	3	4	5	6	7	8	9
0·000	0000	0001	0001	0002	0003	0003	0004	0004	0004	0005
0·001	0005	0006	0006	0007	0007	0008	0008	0009	0010	0010
0·002	0011	0011	0012	0012	0013	0013	0014	0014	0015	0015
0·003	0016	0016	0017	0017	0018	0019	0019	0020	0021	0021
0·004	0022	0022	0023	0023	0024	0024	0025	0025	0026	0026
0·005	0027	0027	0028	0028	0029	0029	0030	0030	0031	0031
0·006	0032	0032	0033	0033	0034	0034	0035	0036	0036	0037
0·007	0037	0038	0038	0039	0039	0040	0040	0041	0041	0042
0·008	0042	0043	0043	0044	0045	0045	0046	0046	0047	0047
0·009	0048	0048	0049	0049	0050	0050	0051	0051	0052	0052
0·010	0053	0054	0054	0055	0055	0056	0056	0057	0057	0058
0·011	0058	0059	0059	0060	0060	0061	0061	0062	0062	0063
0·012	0064	0064	0065	0065	0066	0066	0067	0067	0068	0068
0·013	0069	0069	0070	0070	0071	0072	0072	0073	0073	0074
0·014	0074	0075	0075	0076	0076	0077	0077	0078	0078	0079
0·015	0080	0080	0081	0081	0082	0082	0083	0083	0084	0084
0·016	0085	0085	0086	0086	0087	0087	0088	0089	0089	0090
0·017	0090	0091	0091	0092	0092	0093	0093	0094	0094	0095
0·018	0095	0096	0096	0097	0098	0098	0099	0099	0100	0100
0·019	0101	0101	0102	0103	0103	0104	0104	0104	0105	0105
0·020	0106	0107	0107	0108	0108	0109	0109	0110	0110	0111
0·021	0111	0112	0112	0113	0113	0114	0114	0115	0116	0116
0·022	0117	0117	0118	0119	0119	0119	0120	0120	0121	0121
0·023	0122	0122	0123	0123	0124	0125	0125	0126	0126	0127
0·024	0127	0128	0128	0129	0129	0130	0130	0131	0131	0132
0·025	0133	0133	0134	0134	0135	0135	0136	0136	0137	0137
0·026	0138	0138	0139	0139	0140	0140	0141	0142	0142	0143
0·027	0143	0144	0144	0145	0145	0146	0146	0147	0147	0148
0·028	0148	0149	0149	0150	0151	0151	0152	0152	0153	0153
0·029	0154	0154	0155	0155	0156	0156	0157	0157	0158	0158
0·030	0159	0160	0160	0161	0161	0162	0162	0163	0163	0164
0·031	0164	0165	0165	0166	0166	0167	0167	0168	0169	0169
0·032	0170	0170	0171	0171	0172	0172	0173	0173	0174	0174
0·033	0175	0176	0176	0176	0177	0178	0178	0179	0179	0180
0·034	0180	0181	0181	0182	0182	0183	0183	0184	0184	0185
0·035	0186	0186	0187	0187	0188	0188	0189	0189	0190	0190
0·036	0191	0191	0192	0192	0193	0193	0194	0195	0195	0196
0·037	0196	0197	0197	0198	0198	0199	0199	0200	0200	0201
0·038	0201	0202	0202	0203	0204	0204	0205	0205	0206	0206
0·039	0207	0207	0208	0208	0209	0209	0210	0210	0211	0211

Table LXXXIX.—NaCl to Na_2O.—*continued.*

Grm. NaCl.	Grm. Na_2O.									
	0	1	2	3	4	5	6	7	8	9
0·040	0212	0213	0213	0214	0214	0215	0215	0216	0216	0217
0·041	0217	0218	0218	0219	0219	0220	0220	0221	0222	0222
0·042	0223	0223	0224	0224	0225	0225	0226	0226	0227	0227
0·043	0228	0228	0229	0229	0230	0231	0231	0232	0232	0233
0·044	0233	0234	0234	0235	0235	0236	0236	0237	0237	0238
0·045	0239	0239	0240	0240	0241	0241	0242	0242	0243	0243
0·046	0244	0244	0245	0245	0246	0246	0247	0248	0248	0249
0·047	0249	0250	0250	0251	0251	0252	0252	0253	0253	0254
0·048	0254	0255	0255	0256	0257	0257	0258	0258	0259	0259
0·049	0260	0260	0261	0261	0262	0262	0263	0263	0264	0264
0·050	0265	0265	0266	0267	0267	0268	0268	0269	0269	0270
0·051	0270	0271	0271	0272	0272	0273	0273	0274	0275	0275
0·052	0276	0276	0277	0277	0278	0278	0279	0279	0280	0280
0·053	0281	0281	0282	0282	0283	0284	0284	0285	0285	0286
0·054	0286	0287	0288	0288	0289	0289	0290	0290	0291	0292
0·055	0292	0293	0293	0294	0294	0295	0295	0296	0296	0297
0·056	0297	0297	0298	0298	0299	0299	0300	0301	0301	0302
0·057	0302	0303	0303	0304	0304	0305	0305	0306	0306	0307
0·058	0307	0309	0309	0310	0310	0310	0311	0311	0312	0312
0·059	0313	0313	0314	0314	0315	0315	0316	0316	0317	0317
0·060	0318	0319	0319	0320	0320	0321	0321	0322	0322	0323
0·061	0323	0324	0324	0325	0325	0326	0326	0327	0328	0328
0·062	0329	0329	0330	0330	0331	0331	0332	0332	0333	0333
0·063	0334	0334	0335	0335	0336	0337	0337	0338	0338	0339
0·064	0339	0340	0340	0341	0341	0342	0342	0343	0343	0344
0·065	0345	0345	0346	0346	0347	0347	0348	0348	0349	0349
0·066	0350	0350	0351	0351	0352	0352	0353	0354	0354	0355
0·067	0355	0356	0356	0357	0357	0358	0358	0359	0359	0360
0·068	0360	0361	0361	0362	0363	0363	0364	0364	0365	0365
0·069	0366	0366	0367	0367	0368	0368	0369	0369	0370	0370
0·070	0371	0372	0372	0373	0373	0374	0374	0375	0375	0376
0·071	0376	0377	0377	0378	0378	0379	0379	0380	0381	0381
0·072	0382	0382	0383	0383	0384	0384	0385	0385	0386	0386
0·073	0387	0387	0388	0388	0389	0390	0390	0391	0391	0392
0·074	0392	0393	0393	0394	0394	0395	0395	0396	0396	0397
0·075	0398	0398	0399	0399	0400	0400	0401	0401	0402	0402
0·076	0403	0403	0404	0404	0405	0405	0406	0407	0407	0408
0·077	0408	0409	0409	0410	0410	0411	0411	0412	0412	0413
0·078	0413	0414	0414	0415	0416	0416	0417	0417	0418	0418
0·079	0419	0419	0420	0420	0421	0421	0422	0422	0423	0423
0·080	0424	0425	0425	0426	0426	0427	0427	0428	0428	0429
0·081	0429	0430	0430	0431	0431	0432	0432	0433	0434	0434
0·082	0435	0435	0436	0436	0437	0437	0438	0438	0439	0439
0·083	0440	0440	0441	0441	0442	0443	0443	0444	0444	0445
0·084	0445	0446	0446	0447	0447	0448	0448	0449	0449	0450

Table LXXXIX.—NaCl to Na_2O.—*continued.*

Grm. NaCl.	Grm. Na_2O.									
	0	1	2	3	4	5	6	7	8	9
0·085	0451	0451	0452	0452	0453	0453	0454	0454	0455	0455
0·086	0456	0456	0457	0457	0458	0458	0459	0460	0460	0461
0·087	0461	0462	0462	0463	0463	0464	0464	0465	0465	0466
0·088	0466	0467	0467	0468	0469	0469	0470	0470	0471	0471
0·089	0472	0472	0473	0473	0474	0474	0475	0475	0476	0476
0·090	0477	0478	0478	0479	0479	0480	0480	0481	0481	0482
0·091	0482	0483	0483	0484	0484	0485	0485	0486	0487	0487
0·092	0488	0488	0489	0489	0490	0490	0491	0491	0492	0492
0·093	0493	0493	0494	0494	0495	0496	0496	0497	0497	0498
0·094	0498	0499	0499	0500	0500	0501	0501	0502	0502	0503
0·095	0504	0504	0505	0505	0506	0506	0507	0507	0508	0508
0·096	0509	0509	0510	0510	0511	0511	0512	0513	0513	0514
0·097	0514	0515	0515	0516	0516	0517	0517	0518	0518	0519
0·098	0519	0520	0520	0521	0522	0522	0523	0523	0524	0524
0·099	0525	0525	0526	0526	0527	0527	0528	0528	0529	0529
0·100	0530	0531	0531	0532	0532	0533	0533	0534	0534	0535
0·101	0535	0536	0536	0537	0537	0538	0538	0539	0540	0540
0·102	0541	0541	0542	0542	0543	0543	0544	0544	0545	0545
0·103	0546	0546	0547	0548	0548	0549	0549	0550	0550	0551
0·104	0551	0552	0552	0553	0553	0554	0554	0555	0555	0556
0·105	0557	0557	0558	0558	0559	0559	0560	0560	0561	0561
0·106	0562	0562	0563	0563	0564	0564	0565	0566	0566	0567
0·107	0567	0568	0568	0569	0569	0570	0570	0571	0571	0572
0·108	0572	0573	0573	0574	0575	0575	0576	0576	0577	0577
0·109	0578	0578	0579	0579	0580	0580	0581	0581	0582	0582
0·110	0583	0583	0584	0585	0585	0586	0586	0587	0587	0588
0·111	0588	0589	0589	0590	0591	0591	0592	0592	0593	0594
0·112	0594	0595	0595	0596	0596	0597	0597	0598	0598	0599
0·113	0599	0600	0600	0601	0601	0602	0602	0603	0603	0604
0·114	0604	0605	0605	0606	0606	0607	0607	0608	0608	0609
0·115	0610	0611	0611	0612	0612	0613	0613	0614	0614	0615
0·116	0615	0616	0616	0617	0617	0618	0618	0619	0619	0620
0·117	0620	0621	0621	0622	0622	0623	0623	0624	0624	0625
0·118	0625	0626	0626	0627	0628	0628	0629	0629	0630	0630
0·119	0631	0631	0632	0632	0633	0633	0634	0634	0635	0635
0·120	0636	0637	0637	0638	0638	0639	0639	0640	0640	0641
0·121	0641	0642	0642	0643	0643	0644	0645	0645	0646	0646
0·122	0647	0647	0648	0648	0649	0649	0650	0650	0651	0651
0·123	0652	0652	0653	0653	0654	0654	0655	0656	0656	0657
0·124	0657	0658	0658	0659	0659	0660	0660	0661	0661	0662
0·125	0663	0663	0664	0664	0665	0665	0666	0666	0667	0667
0·126	0668	0668	0669	0669	0670	0670	0671	0672	0672	0673
0·127	0673	0674	0674	0675	0675	0676	0676	0677	0677	0678
0·128	0678	0679	0680	0681	0681	0682	0682	0683	0683	0684
0·129	0684	0685	0685	0686	0686	0687	0687	0688	0688	0689

Table LXXXIX.—NaCl to Na_2O.—*continued.*

Grm. NaCl.	Grm. Na_2O.									
	0	1	2	3	4	5	6	7	8	9
0·130	0689	0690	0690	0691	0691	0692	0692	0693	0693	0694
0·131	0694	0695	0695	0696	0696	0697	0697	0698	0698	0699
0·132	0700	0700	0701	0701	0702	0702	0703	0703	0704	0704
0·133	0705	0705	0706	0706	0707	0707	0708	0709	0709	0710
0·134	0710	0711	0711	0712	0712	0713	0713	0714	0714	0715
0·135	0716	0716	0717	0717	0718	0718	0719	0719	0720	0720
0·136	0721	0721	0722	0722	0723	0723	0724	0724	0725	0726
0·137	0726	0727	0727	0727	0728	0728	0729	0729	0730	0731
0·138	0731	0732	0732	0733	0733	0734	0734	0735	0735	0736
0·139	0736	0737	0737	0738	0739	0739	0740	0740	0741	0741
0·140	0742	0742	0743	0743	0744	0744	0745	0745	0746	0746
0·141	0747	0747	0748	0748	0749	0749	0750	0751	0751	0752
0·142	0752	0753	0753	0754	0754	0755	0755	0756	0756	0757
0·143	0757	0758	0758	0759	0759	0760	0761	0761	0762	0762
0·144	0763	0763	0764	0764	0765	0765	0766	0766	0767	0768
0·145	0768	0769	0770	0770	0771	0771	0772	0772	0773	0773
0·146	0774	0774	0775	0775	0776	0776	0777	0778	0778	0779
0·147	0779	0780	0780	0781	0781	0782	0782	0783	0783	0784
0·148	0784	0785	0785	0786	0786	0787	0788	0788	0789	0789
0·149	0790	0790	0791	0791	0792	0792	0793	0793	0794	0794
0·150	0795	0795	0796	0797	0797	0798	0798	0799	0799	0800
0·151	0800	0801	0801	0802	0802	0803	0803	0804	0805	0805
0·152	0806	0806	0807	0807	0808	0808	0809	0809	0810	0810
0·153	0811	0811	0812	0813	0813	0814	0814	0815	0815	0816
0·154	0816	0817	0817	0818	0818	0819	0819	0820	0820	0821
0·155	0821	0822	0823	0823	0824	0824	0285	0825	0826	0826
0·156	0827	0827	0828	0828	0829	0829	0830	0831	0831	0832
0·157	0832	0833	0833	0834	0834	0835	0835	0836	0836	0837
0·158	0837	0838	0838	0839	0840	0840	0841	0841	0842	0842
0·159	0843	0843	0844	0844	0845	0845	0846	0846	0847	0848
0·160	0848	0849	0849	0850	0850	0851	0851	0852	0852	0853
0·161	0853	0854	0854	0855	0856	0856	0857	0857	0858	0859
0·162	0859	0859	0860	0860	0861	0861	0862	0862	0863	0863
0·163	0864	0864	0865	0866	0866	0867	0867	0868	0868	0869
0·164	0869	0870	0870	0871	0871	0872	0872	0873	0874	0874
0·165	0875	0875	0876	0876	0877	0877	0878	0878	0879	0879
0·166	0880	0880	0881	0881	0882	0882	0883	0884	0884	0885
0·167	0885	0886	0886	0887	0887	0888	0888	0889	0889	0890
0·168	0890	0891	0891	0892	0892	0893	0894	0894	0895	0895
0·169	0896	0896	0897	0897	0898	0898	0899	0899	0900	0900
0·170	0901	0902	0902	0903	0903	0904	0904	0905	0905	0906
0·171	0906	0907	0907	0908	0908	0909	0909	0910	0911	0911
0·172	0912	0912	0913	0913	0914	0914	0915	0915	0916	0916
0·173	0917	0917	0918	0918	0919	0919	0920	0921	0921	0922
0·174	0922	0923	0923	0924	0924	0925	0925	0926	0926	0927

Table LXXXIX.—NaCl to Na_2O.—*continued.*

Grm. NaCl.	Grm. Na_2O.									
	0	1	2	3	4	5	6	7	8	9
0·175	0928	0928	0929	0929	0930	0930	0931	0931	0932	0932
0·176	0933	0933	0934	0934	0935	0935	0936	0937	0937	0938
0·177	0938	0939	0939	0940	0940	0941	0941	0942	0942	0943
0·178	0943	0944	0944	0945	0945	0946	0947	0948	0948	0949
0·179	0949	0950	0950	0951	0951	0952	0952	0953	0953	0954
0·180	0954	0955	0955	0956	0956	0957	0957	0958	0958	0959
0·181	0959	0960	0960	0961	0961	0962	0962	0963	0964	0964
0·182	0965	0965	0966	0966	0967	0967	0968	0968	0969	0969
0·183	0970	0970	0971	0971	0972	0973	0973	0974	0974	0975
0·184	0975	0976	0976	0977	0977	0978	0978	0979	0979	0980
0·185	0981	0981	0982	0982	0983	0983	0984	0984	0985	0985
0·186	0986	0986	0987	0987	0988	0988	0989	0990	0990	0991
0·187	0991	0992	0992	0993	0993	0994	0994	0995	0995	0996
0·188	0996	0997	0997	0998	0999	0999	1000	1000	1001	1001
0·189	1002	1002	1003	1003	1003	1004	1004	1005	1005	1006
0·190	1007	1007	1008	1008	1009	1009	1010	1010	1011	1012
0·191	1012	1013	1013	1014	1014	1015	1015	1016	1017	1017
0·192	1018	1018	1019	1019	1020	1020	1021	1021	1022	1022
0·193	1023	1023	1024	1025	1025	1026	1026	1027	1027	1028
0·194	1028	1029	1029	1030	1030	1031	1031	1032	1032	1033
0·195	1034	1034	1035	1035	1036	1036	1037	1037	1038	1038
0·196	1039	1039	1040	1040	1041	1041	1042	1042	1043	1044
0·197	1044	1045	1045	1046	1046	1047	1047	1048	1048	1049
0·198	1049	1050	1051	1051	1052	1052	1053	1053	1054	1054
0·199	1055	1055	1056	1056	1056	1057	1057	1058	1058	1059

Table XC.—Conversion of Grms. of Magnesium Pyrophosphate ($Mg_2P_2O_7$) into Grms. of Magnesium Oxide (MgO).

(FACTOR 0·362.)

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·000	..	..	0001	0001	0001	0002	0002	0003	0003	0003
0·001	0004	0004	0004	0005	0005	0005	0006	0006	0007	0007
0·002	0007	0008	0008	0008	0009	0009	0009	0010	0010	0010
0·003	0011	0011	0012	0012	0012	0013	0013	0013	0014	0014
0·004	0014	0015	0015	0015	0016	0016	0017	0017	0017	0018
0·005	0018	0018	0019	0019	0020	0020	0020	0021	0021	0021
0·006	0022	0022	0022	0023	0023	0024	0024	0024	0025	0025
0·007	0025	0026	0026	0026	0027	0027	0028	0028	0028	0029
0·008	0029	0029	0029	0030	0030	0031	0031	0031	0032	0032
0·009	0033	0033	0033	0034	0034	0034	0035	0035	0035	0036
0·010	0036	0037	0037	0037	0038	0038	0038	0039	0039	0039
0·011	0040	0040	0041	0041	0041	0042	0042	0042	0043	0043
0·012	0043	0044	0044	0045	0045	0045	0046	0046	0046	0047
0·013	0047	0047	0048	0048	0049	0049	0049	0050	0050	0050
0·014	0051	0051	0051	0052	0052	0052	0053	0053	0054	0054
0·015	0054	0055	0055	0055	0056	0056	0056	0057	0057	0058
0·016	0058	0058	0059	0059	0059	0060	0060	0060	0061	0061
0·017	0062	0062	0062	0063	0063	0063	0064	0064	0064	0065
0·018	0065	0066	0066	0066	0067	0067	0067	0068	0068	0068
0·019	0069	0069	0070	0070	0070	0071	0071	0071	0072	0072
0·020	0072	0073	0073	0073	0074	0074	0075	0075	0075	0076
0·021	0076	0076	0077	0077	0078	0078	0078	0079	0079	0079
0·022	0080	0080	0080	0081	0081	0081	0082	0082	0083	0083
0·023	0083	0084	0084	0084	0085	0085	0085	0086	0086	0087
0·024	0087	0087	0088	0088	0088	0089	0089	0089	0090	0090
0·025	0091	0091	0091	0092	0092	0092	0093	0093	0093	0094
0·026	0094	0094	0095	0095	0096	0096	0096	0097	0097	0097
0·027	0098	0098	0098	0099	0099	0100	0100	0100	0101	0101
0·028	0101	0102	0102	0102	0103	0103	0104	0104	0104	0105
0·029	0105	0105	0106	0106	0107	0107	0107	0108	0108	0108
0·030	0109	0109	0109	0110	0110	0110	0111	0111	0111	0112
0·031	0112	0113	0113	0113	0114	0114	0114	0115	0115	0115
0·032	0116	0116	0117	0117	0117	0118	0118	0118	0119	0119
0·033	0119	0120	0120	0121	0121	0121	0122	0122	0122	0123
0·034	0123	0123	0123	0124	0125	0125	0125	0126	0126	0126
0·035	0127	0127	0127	0128	0128	0129	0129	0129	0130	0130
0·036	0130	0131	0131	0131	0132	0132	0132	0133	0133	0134
0·037	0134	0134	0135	0135	0135	0136	0136	0136	0137	0137
0·038	0138	0138	0138	0139	0139	0139	0140	0140	0140	0141
0·039	0141	0142	0142	0142	0143	0143	0143	0144	0144	0144

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·040	0145	0145	0146	0146	0146	0147	0147	0147	0148	0148
0·041	0148	0149	0149	0149	0150	0150	0151	0151	0151	0152
0·042	0152	0152	0153	0153	0153	0154	0154	0155	0155	0155
0·043	0156	0156	0156	0157	0157	0157	0158	0158	0159	0159
0·044	0159	0160	0160	0160	0161	0161	0161	0162	0162	0163
0·045	0163	0163	0164	0164	0164	0165	0165	0165	0166	0166
0·046	0167	0167	0167	0168	0168	0168	0169	0169	0169	0170
0·047	0170	0171	0171	0171	0172	0172	0172	0173	0173	0173
0·048	0174	0174	0174	0175	0175	0176	0176	0176	0177	0177
0·049	0177	0178	0178	0178	0179	0179	0180	0180	0180	0181
0·050	0181	0181	0182	0182	0182	0183	0183	0184	0184	0184
0·051	0185	0185	0185	0186	0186	0186	0187	0187	0188	0188
0·052	0188	0189	0189	0189	0190	0190	0190	0191	0191	0191
0·053	0192	0192	0193	0193	0193	0194	0194	0194	0195	0195
0·054	0195	0196	0196	0197	0197	0197	0198	0198	0198	0199
0·055	0199	0199	0200	0200	0201	0201	0201	0202	0202	0202
0·056	0203	0203	0203	0204	0204	0205	0205	0205	0206	0206
0·057	0206	0207	0207	0207	0208	0208	0209	0209	0209	0210
0·058	0210	0210	0211	0211	0211	0212	0212	0212	0213	0213
0·059	0214	0214	0214	0215	0215	0215	0216	0216	0216	0217
0·060	0217	0218	0218	0218	0219	0219	0219	0220	0220	0220
0·061	0221	0221	0222	0222	0222	0223	0223	0223	0224	0224
0·062	0224	0225	0225	0226	0226	0226	0227	0227	0227	0228
0·063	0228	0228	0229	0229	0230	0230	0230	0231	0231	0231
0·064	0232	0232	0232	0233	0233	0234	0234	0234	0235	0235
0·065	0235	0236	0236	0236	0237	0237	0237	0238	0238	0238
0·066	0239	0239	0240	0240	0240	0241	0241	0242	0242	0242
0·067	0243	0243	0243	0244	0244	0244	0245	0245	0245	0246
0·068	0246	0247	0247	0247	0248	0248	0248	0249	0249	0249
0·069	0250	0250	0251	0251	0251	0252	0252	0252	0253	0253
0·070	0253	0254	0254	0254	0255	0255	0256	0256	0256	0257
0·071	0257	0257	0258	0258	0258	0259	0259	0260	0260	0260
0·072	0261	0261	0261	0262	0262	0262	0263	0263	0264	0264
0·073	0264	0265	0265	0265	0266	0266	0266	0267	0267	0268
0·074	0268	0268	0269	0269	0269	0270	0270	0270	0271	0271
0·075	0272	0272	0272	0273	0273	0273	0274	0274	0274	0275
0·076	0275	0275	0276	0276	0277	0277	0277	0278	0278	0278
0·077	0279	0279	0279	0280	0280	0281	0281	0281	0282	0282
0·078	0282	0283	0283	0283	0284	0284	0285	0285	0285	0286
0·079	0286	0286	0287	0287	0287	0288	0288	0289	0289	0289
0·080	0290	0290	0290	0291	0291	0291	0292	0292	0292	0293
0·081	0293	0294	0294	0294	0295	0295	0295	0296	0296	0296
0·082	0297	0297	0298	0298	0298	0299	0299	0299	0300	0300
0·083	0300	0301	0301	0302	0302	0302	0303	0303	0303	0304
0·084	0304	0304	0305	0305	0306	0306	0306	0307	0307	0307

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·085	0308	0308	0308	0309	0309	0310	0310	0310	0311	0311
0·086	0311	0312	0312	0312	0313	0313	0313	0314	0314	0315
0·087	0315	0315	0316	0316	0316	0317	0317	0317	0318	0318
0·088	0319	0319	0319	0320	0320	0320	0321	0321	0321	0322
0·089	0322	0323	0323	0323	0324	0324	0324	0325	0325	0325
0·090	0326	0326	0326	0327	0327	0328	0328	0328	0329	0329
0·091	0329	0330	0330	0331	0331	0331	0332	0332	0332	0333
0·092	0333	0333	0334	0334	0334	0335	0335	0336	0336	0336
0·093	0337	0337	0337	0338	0338	0338	0339	0339	0340	0340
0·094	0340	0341	0341	0341	0342	0342	0342	0343	0343	0344
0·095	0344	0344	0345	0345	0345	0346	0346	0346	0347	0347
0·096	0348	0348	0348	0349	0349	0349	0350	0350	0350	0351
0·097	0351	0352	0352	0352	0353	0353	0353	0354	0354	0354
0·098	0355	0355	0355	0356	0356	0357	0357	0357	0358	0358
0·099	0358	0359	0359	0359	0360	0360	0361	0361	0361	0362
0·100	0362	0362	0363	0363	0363	0364	0364	0365	0365	0365
0·101	0366	0366	0366	0367	0367	0367	0368	0368	0369	0369
0·102	0369	0370	0370	0370	0371	0371	0371	0372	0372	0372
0·103	0373	0373	0374	0374	0374	0375	0375	0375	0376	0376
0·104	0376	0377	0377	0378	0378	0378	0379	0379	0379	0380
0·105	0380	0380	0381	0381	0382	0382	0382	0383	0383	0383
0·106	0384	0384	0384	0385	0385	0386	0386	0386	0387	0387
0·107	0387	0388	0388	0388	0389	0389	0389	0390	0390	0391
0·108	0391	0391	0392	0392	0392	0393	0393	0394	0394	0394
0·109	0395	0395	0395	0396	0396	0396	0397	0397	0397	0398
0·110	0398	0399	0399	0399	0400	0400	0400	0401	0401	0401
0·111	0402	0402	0403	0403	0403	0404	0404	0404	0405	0405
0·112	0405	0406	0406	0407	0407	0407	0408	0408	0408	0409
0·113	0409	0409	0410	0410	0411	0411	0411	0412	0412	0412
0·114	0413	0413	0413	0414	0414	0414	0415	0415	0416	0416
0·115	0416	0417	0417	0417	0418	0418	0418	0419	0419	0420
0·116	0420	0420	0421	0421	0421	0422	0422	0422	0423	0423
0·117	0424	0424	0424	0425	0425	0425	0426	0426	0426	0427
0·118	0427	0428	0428	0428	0429	0429	0429	0430	0430	0430
0·119	0431	0431	0432	0432	0432	0433	0433	0433	0434	0434
0·120	0434	0435	0435	0435	0436	0436	0437	0437	0437	0438
0·121	0438	0438	0439	0439	0439	0440	0440	0441	0441	0441
0·122	0442	0442	0442	0443	0443	0443	0444	0444	0445	0445
0·123	0445	0446	0446	0446	0447	0447	0447	0448	0448	0449
0·124	0449	0449	0450	0450	0450	0451	0451	0451	0452	0452
0·125	0453	0453	0453	0454	0454	0454	0455	0455	0455	0456
0·126	0456	0456	0457	0457	0458	0458	0458	0459	0459	0459
0·127	0460	0460	0460	0461	0461	0462	0462	0462	0463	0463
0·128	0463	0464	0464	0464	0465	0465	0466	0466	0466	0467
0·129	0467	0467	0468	0468	0468	0469	0469	0470	0470	0470

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·130	0471	0471	0471	0472	0472	0472	0473	0473	0473	0474
0·131	0474	0475	0475	0475	0476	0476	0476	0477	0477	0477
0·132	0478	0478	0479	0479	0479	0480	0480	0480	0481	0481
0·133	0481	0482	0482	0483	0483	0483	0484	0484	0484	0485
0·134	0485	0485	0486	0486	0487	0487	0487	0488	0488	0488
0·135	0489	0489	0489	0490	0490	0491	0491	0491	0492	0492
0·136	0492	0493	0493	0493	0494	0494	0494	0495	0495	0496
0·137	0496	0496	0497	0497	0497	0498	0498	0498	0499	0499
0·138	0500	0500	0500	0501	0501	0501	0502	0502	0502	0503
0·139	0503	0504	0504	0504	0505	0505	0505	0506	0506	0506
0·140	0507	0507	0508	0508	0508	0509	0509	0509	0510	0510
0·141	0510	0511	0511	0512	0512	0512	0513	0513	0513	0514
0·142	0514	0515	0515	0515	0516	0516	0516	0517	0517	0518
0·143	0518	0518	0519	0519	0519	0520	0520	0520	0521	0521
0·144	0521	0522	0522	0523	0523	0523	0524	0524	0524	0525
0·145	0525	0526	0526	0526	0527	0527	0527	0528	0528	0528
0·146	0529	0529	0529	0530	0530	0531	0531	0531	0532	0532
0·147	0532	0533	0533	0533	0534	0534	0534	0535	0535	0535
0·148	0536	0536	0536	0537	0537	0538	0538	0538	0539	0539
0·149	0539	0540	0540	0540	0541	0541	0542	0542	0542	0543
0·150	0543	0543	0544	0544	0544	0545	0545	0546	0546	0546
0·151	0547	0547	0547	0548	0548	0548	0549	0549	0550	0550
0·152	0550	0551	0551	0551	0551	0552	0552	0553	0553	0553
0·153	0554	0554	0555	0555	0555	0556	0556	0556	0557	0557
0·154	0557	0558	0558	0559	0559	0559	0560	0560	0560	0561
0·155	0561	0561	0562	0562	0563	0563	0563	0564	0564	0564
0·156	0565	0565	0565	0566	0566	0567	0567	0567	0568	0568
0·157	0568	0569	0569	0569	0570	0570	0571	0571	0571	0572
0·158	0572	0572	0573	0573	0573	0574	0574	0574	0575	0575
0·159	0576	0576	0576	0577	0577	0577	0578	0578	0578	0579
0·160	0579	0580	0580	0580	0581	0581	0581	0582	0582	0582
0·161	0583	0583	0584	0584	0584	0585	0585	0585	0586	0586
0·162	0586	0587	0587	0588	0588	0588	0589	0589	0589	0590
0·163	0590	0590	0591	0591	0592	0592	0592	0593	0593	0593
0·164	0594	0594	0594	0595	0595	0595	0596	0596	0597	0597
0·165	0597	0598	0598	0598	0599	0599	0599	0600	0600	0601
0·166	0601	0601	0602	0602	0602	0603	0603	0603	0604	0604
0·167	0605	0605	0605	0606	0606	0606	0607	0607	0607	0608
0·168	0608	0609	0609	0609	0610	0610	0610	0611	0611	0611
0·169	0612	0612	0613	0613	0613	0614	0614	0614	0615	0615
0·170	0615	0616	0616	0616	0617	0617	0618	0618	0618	0619
0·171	0619	0619	0620	0620	0620	0621	0621	0622	0622	0622
0·172	0623	0623	0623	0624	0624	0624	0625	0625	0626	0626
0·173	0626	0627	0627	0627	0628	0628	0628	0629	0629	0630
0·174	0630	0630	0631	0631	0631	0632	0632	0633	0633	0633

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·175	0634	0634	0634	0635	0635	0635	0636	0636	0636	0637
0·176	0637	0637	0638	0638	0639	0639	0639	0640	0640	0640
0·177	0641	0641	0641	0642	0642	0643	0643	0643	0644	0644
0·178	0645	0645	0645	0646	0646	0646	0647	0647	0647	0648
0·179	0648	0649	0649	0649	0650	0650	0650	0651	0651	0651
0·180	0652	0652	0652	0653	0653	0653	0654	0654	0654	0655
0·181	0655	0656	0656	0656	0657	0657	0657	0658	0658	0658
0·182	0659	0659	0660	0660	0660	0661	0661	0661	0662	0662
0·183	0662	0663	0663	0664	0664	0664	0665	0665	0665	0666
0·184	0666	0666	0667	0667	0668	0668	0668	0669	0669	0669
0·185	0670	0670	0670	0671	0671	0672	0672	0672	0673	0673
0·186	0673	0674	0674	0674	0675	0675	0675	0676	0676	0677
0·187	0677	0677	0678	0678	0678	0679	0679	0679	0680	0680
0·188	0681	0681	0681	0682	0682	0682	0683	0683	0683	0684
0·189	0684	0685	0685	0685	0686	0686	0686	0687	0687	0687
0·190	0688	0688	0689	0689	0689	0690	0690	0690	0691	0691
0·191	0691	0692	0692	0693	0693	0693	0694	0694	0694	0695
0·192	0695	0695	0696	0696	0696	0697	0697	0698	0698	0698
0·193	0699	0699	0699	0700	0700	0700	0701	0701	0702	0702
0·194	0702	0703	0703	0703	0704	0704	0704	0705	0705	0706
0·195	0706	0706	0707	0707	0707	0708	0708	0708	0709	0709
0·196	0710	0710	0710	0711	0711	0711	0712	0712	0712	0713
0·197	0713	0714	0714	0714	0715	0715	0715	0716	0716	0716
0·198	0717	0717	0717	0718	0718	0719	0719	0719	0720	0720
0·199	0720	0721	0721	0721	0722	0722	0723	0723	0723	0724
0·200	0724	0724	0725	0725	0725	0726	0726	0727	0727	0727
0·201	0728	0728	0728	0729	0729	0729	0730	0730	0731	0731
0·202	0731	0732	0732	0732	0733	0733	0733	0734	0734	0734
0·203	0735	0735	0736	0736	0736	0737	0737	0737	0738	0738
0·204	0738	0739	0739	0740	0740	0740	0741	0741	0741	0742
0·205	0742	0742	0743	0743	0744	0744	0744	0745	0745	0745
0·206	0746	0746	0746	0747	0747	0748	0748	0748	0749	0749
0·207	0749	0750	0750	0750	0751	0751	0751	0752	0752	0753
0·208	0753	0753	0754	0754	0754	0755	0755	0755	0756	0756
0·209	0757	0757	0757	0758	0758	0758	0759	0759	0759	0760
0·210	0760	0760	0761	0761	0761	0762	0762	0763	0763	0763
0·211	0764	0764	0765	0765	0765	0766	0766	0766	0767	0767
0·212	0767	0768	0768	0769	0769	0769	0770	0770	0770	0771
0·213	0771	0771	0772	0772	0773	0773	0773	0774	0774	0774
0·214	0775	0775	0775	0776	0776	0776	0777	0777	0778	0778
0·215	0778	0779	0779	0779	0780	0780	0780	0781	0781	0782
0·216	0782	0782	0783	0783	0783	0784	0784	0784	0785	0785
0·217	0786	0786	0786	0787	0787	0787	0788	0788	0788	0789
0·218	0789	0790	0790	0790	0791	0791	0791	0792	0792	0792
0·219	0793	0793	0794	0794	0794	0794	0795	0795	0795	0796

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·220	0796	0797	0797	0797	0798	0798	0799	0799	0799	0800
0·221	0800	0800	0801	0801	0801	0802	0802	0803	0803	0803
0·222	0804	0804	0804	0805	0805	0805	0806	0806	0807	0807
0·223	0807	0808	0808	0808	0809	0809	0809	0810	0810	0811
0·224	0811	0811	0812	0812	0812	0813	0813	0813	0814	0814
0·225	0815	0815	0815	0816	0816	0816	0817	0817	0817	0818
0·226	0818	0818	0819	0819	0820	0820	0820	0821	0821	0821
0·227	0822	0822	0822	0823	0823	0824	0824	0824	0825	0825
0·228	0825	0826	0826	0826	0827	0827	0828	0828	0828	0829
0·229	0829	0829	0830	0830	0830	0831	0831	0831	0832	0832
0·230	0833	0833	0833	0834	0834	0834	0835	0835	0835	0836
0·231	0836	0837	0837	0837	0838	0838	0838	0839	0839	0839
0·232	0840	0840	0841	0841	0841	0842	0842	0842	0843	0843
0·233	0843	0844	0844	0845	0845	0845	0846	0846	0846	0847
0·234	0847	0847	0848	0848	0849	0849	0849	0850	0850	0850
0·235	0851	0851	0851	0852	0852	0853	0853	0853	0854	0854
0·236	0854	0855	0855	0855	0856	0856	0856	0857	0857	0858
0·237	0858	0858	0859	0859	0859	0860	0860	0860	0861	0861
0·238	0862	0862	0862	0863	0863	0863	0864	0864	0864	0865
0·239	0865	0866	0866	0866	0867	0867	0867	0868	0868	0868
0·240	0869	0869	0870	0870	0870	0871	0871	0871	0872	0872
0·241	0872	0873	0873	0874	0874	0874	0875	0875	0875	0876
0·242	0876	0876	0877	0877	0877	0878	0878	0879	0879	0879
0·243	0880	0880	0880	0881	0881	0881	0882	0882	0883	0883
0·244	0883	0884	0884	0884	0885	0885	0885	0886	0886	0887
0·245	0887	0887	0888	0888	0888	0889	0889	0889	0890	0890
0·246	0891	0891	0891	0892	0892	0892	0893	0893	0893	0894
0·247	0894	0895	0895	0895	0896	0896	0896	0897	0897	0897
0·248	0898	0898	0898	0899	0899	0900	0900	0900	0901	0901
0·249	0901	0902	0902	0902	0903	0903	0904	0904	0904	0905
0·250	0905	0905	0906	0906	0906	0907	0907	0908	0908	0908
0·251	0909	0909	0909	0910	0910	0910	0911	0911	0912	0912
0·252	0912	0913	0913	0913	0914	0914	0914	0915	0915	0915
0·253	0916	0916	0917	0917	0917	0918	0918	0918	0919	0919
0·254	0919	0920	0920	0920	0921	0921	0921	0922	0922	0923
0·255	0923	0923	0924	0924	0924	0925	0925	0925	0926	0926
0·256	0927	0927	0927	0928	0928	0928	0929	0929	0929	0930
0·257	0930	0931	0931	0931	0932	0932	0932	0933	0933	0934
0·258	0934	0934	0935	0935	0935	0936	0936	0936	0937	0937
0·259	0938	0938	0938	0939	0939	0939	0940	0940	0940	0941
0·260	0941	0942	0942	0942	0943	0943	0943	0944	0944	0944
0·261	0945	0945	0946	0946	0946	0947	0947	0947	0948	0948
0·262	0948	0949	0949	0950	0950	0950	0951	0951	0951	0952
0·263	0952	0952	0953	0953	0954	0954	0954	0955	0955	0955
0·264	0956	0956	0956	0957	0957	0957	0958	0958	0959	0959

Table XC.—$Mg_2P_2O_7$ to MgO.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. MgO.									
	0	1	2	3	4	5	6	7	8	9
0·265	0959	0960	0960	0960	0961	0961	0961	0962	0962	0963
0·266	0963	0963	0964	0964	0964	0965	0965	0965	0966	0966
0·267	0966	0967	0967	0967	0968	0968	0968	0969	0969	0969
0·268	0970	0970	0971	0971	0971	0972	0972	0972	0973	0973
0·269	0973	0974	0974	0975	0975	0975	0976	0976	0976	0977
0·270	0977	0977	0978	0978	0979	0979	0979	0980	0980	0980
0·271	0981	0981	0981	0982	0982	0983	0983	0983	0984	0984
0·272	0984	0985	0985	0985	0986	0986	0987	0987	0987	0988
0·273	0988	0988	0989	0989	0989	0990	0990	0991	0991	0991
0·274	0992	0992	0992	0993	0993	0993	0994	0994	0995	0995
0·275	0996	0996	0997	0997	0997	0998	0998	0998	0999	0999
0·276	0999	1000	1000	1000	1001	1001	1001	1002	1002	1002
0·277	1003	1003	1003	1004	1004	1005	1005	1005	1006	1006
0·278	1006	1007	1007	1007	1008	1008	1009	1009	1009	1010
0·279	1010	1010	1011	1011	1011	1012	1012	1013	1013	1013
0·280	1014	1014	1014	1015	1015	1015	1016	1016	1017	1017
0·281	1017	1018	1018	1018	1019	1019	1019	1020	1020	1020
0·282	1021	1021	1022	1022	1022	1023	1023	1023	1024	1024
0·283	1024	1025	1025	1026	1026	1026	1027	1027	1027	1028
0·284	1028	1028	1029	1029	1030	1030	1030	1031	1031	1031
0·285	1032	1032	1032	1033	1033	1034	1034	1034	1035	1035
0·286	1035	1036	1036	1036	1037	1037	1037	1038	1038	1039
0·287	1039	1039	1040	1040	1040	1041	1041	1041	1042	1042
0·288	1043	1043	1043	1044	1044	1044	1045	1045	1045	1046
0·289	1046	1047	1047	1047	1048	1048	1048	1049	1049	1049
0·290	1050	1050	1051	1051	1051	1052	1052	1052	1053	1053
0·291	1053	1054	1054	1055	1055	1055	1056	1056	1056	1057
0·292	1057	1057	1058	1058	1058	1059	1059	1060	1060	1060
0·293	1061	1061	1061	1062	1062	1062	1063	1063	1064	1064
0·294	1064	1065	1065	1065	1066	1066	1066	1067	1067	1068
0·295	1068	1068	1069	1069	1069	1070	1070	1070	1071	1071
0·296	1072	1072	1072	1073	1073	1073	1074	1074	1074	1075
0·297	1075	1076	1076	1076	1077	1077	1077	1078	1078	1078
0·298	1079	1079	1079	1080	1080	1081	1081	1081	1082	1082
0·299	1082	1083	1083	1083	1084	1084	1085	1085	1085	1086

Table XCI.—Conversion of Grms. of Magnesium Pyrophosphate ($Mg_2P_2O_7$) into Grms. Phosphorus Pentoxide (P_2O_5).

(FACTOR 0·638.)

Grm. $Mg_2P_2O_7$.	Grm. P_2O_5.									
	0	1	2	3	4	5	6	7	8	9
0·000	..	0001	0001	0002	0003	0003	0004	0004	0005	0006
0·001	0006	0007	0008	0008	0009	0010	0010	0011	0011	0012
0·002	0013	0013	0014	0015	0015	0016	0017	0017	0018	0019
0·003	0019	0020	0020	0021	0022	0022	0023	0024	0024	0025
0·004	0026	0026	0027	0027	0028	0029	0029	0030	0031	0031
0·005	0032	0033	0033	0034	0034	0035	0036	0036	0037	0038
0·006	0038	0039	0040	0040	0041	0041	0042	0043	0043	0044
0·007	0045	0045	0046	0047	0047	0048	0048	0049	0050	0050
0·008	0051	0052	0052	0053	0054	0055	0055	0056	0056	0057
0·009	0057	0058	0059	0059	0060	0061	0061	0062	0063	0063
0·010	0064	0064	0065	0066	0066	0067	0068	0068	0069	0070
0·011	0070	0071	0071	0072	0073	0073	0074	0075	0075	0076
0·012	0077	0077	0078	0078	0079	0080	0080	0081	0082	0082
0·013	0083	0084	0084	0085	0085	0086	0087	0087	0088	0089
0·014	0089	0090	0091	0091	0092	0093	0093	0094	0094	0095
0·015	0096	0096	0097	0097	0098	0099	0100	0100	0101	0101
0·016	0102	0103	0103	0104	0105	0105	0106	0107	0107	0108
0·017	0108	0109	0110	0110	0111	0112	0112	0113	0114	0114
0·018	0115	0115	0116	0117	0117	0118	0119	0119	0120	0121
0·019	0121	0122	0122	0123	0124	0124	0125	0126	0126	0127
0·020	0128	0128	0129	0130	0130	0131	0131	0132	0133	0133
0·021	0134	0135	0135	0136	0137	0137	0138	0138	0139	0140
0·022	0140	0141	0142	0143	0143	0144	0144	0145	0145	0146
0·023	0147	0147	0148	0149	0149	0150	0151	0151	0152	0152
0·024	0153	0154	0154	0155	0156	0156	0157	0158	0158	0159
0·025	0160	0160	0161	0161	0162	0163	0163	0164	0165	0165
0·026	0166	0167	0167	0168	0168	0169	0170	0170	0171	0172
0·027	0172	0173	0174	0174	0175	0175	0176	0177	0177	0178
0·028	0179	0179	0180	0181	0181	0182	0182	0183	0184	0184
0·029	0185	0186	0186	0187	0188	0189	0189	0189	0190	0191
0·030	0191	0192	0193	0193	0194	0195	0195	0196	0197	0197
0·031	0198	0198	0199	0200	0200	0201	0202	0202	0203	0204
0·032	0204	0205	0205	0206	0207	0207	0208	0209	0209	0210
0·033	0211	0211	0212	0212	0213	0214	0214	0215	0216	0216
0·034	0217	0218	0218	0219	0219	0220	0221	0221	0222	0223
0·035	0223	0224	0225	0225	0226	0226	0227	0228	0228	0229
0·036	0230	0230	0231	0232	0232	0233	0234	0234	0235	0235
0·037	0236	0237	0237	0238	0239	0239	0240	0241	0241	0242
0·038	0242	0243	0244	0244	0245	0246	0246	0247	0248	0248
0·039	0249	0249	0250	0251	0251	0252	0253	0253	0254	0255

Table XCI.—$Mg_2P_2O_7$ to P_2O_5.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. P_2O_5.									
	0	1	2	3	4	5	6	7	8	9
0·040	0255	0256	0256	0257	0258	0258	0259	0260	0260	0261
0·041	0262	0262	0263	0263	0264	0265	0265	0266	0267	0267
0·042	0268	0269	0269	0270	0271	0271	0272	0272	0273	0274
0·043	0274	0275	0276	0276	0277	0278	0278	0279	0279	0280
0·044	0281	0281	0282	0283	0283	0284	0285	0285	0286	0286
0·045	0287	0288	0288	0289	0290	0290	0291	0292	0292	0293
0·046	0293	0294	0295	0295	0296	0297	0297	0298	0299	0299
0·047	0300	0300	0301	0302	0302	0303	0304	0304	0305	0306
0·048	0306	0307	0308	0308	0309	0309	0310	0311	0311	0312
0·049	0313	0313	0314	0315	0315	0316	0316	0317	0318	0318
0·050	0319	0320	0320	0321	0322	0322	0323	0323	0324	0325
0·051	0325	0326	0327	0327	0328	0329	0329	0330	0330	0331
0·052	0332	0332	0333	0334	0334	0335	0336	0336	0337	0338
0·053	0338	0339	0339	0340	0341	0341	0342	0343	0343	0344
0·054	0345	0345	0346	0347	0348	0348	0348	0349	0350	0350
0·055	0351	0352	0352	0353	0353	0354	0355	0355	0356	0357
0·056	0357	0358	0359	0359	0360	0360	0361	0362	0362	0363
0·057	0364	0364	0365	0366	0366	0367	0367	0368	0369	0369
0·058	0370	0371	0371	0372	0373	0373	0374	0375	0375	0376
0·059	0376	0377	0378	0378	0379	0380	0380	0381	0382	0382
0·060	0383	0383	0384	0385	0385	0386	0387	0387	0388	0389
0·061	0389	0390	0390	0391	0392	0392	0393	0394	0394	0395
0·062	0396	0396	0397	0397	0398	0399	0399	0400	0401	0401
0·063	0402	0403	0403	0404	0404	0405	0406	0406	0407	0408
0·064	0408	0409	0410	0410	0411	0412	0412	0413	0413	0414
0·065	0415	0415	0416	0417	0417	0418	0419	0419	0420	0420
0·066	0421	0422	0422	0423	0424	0424	0425	0426	0426	0427
0·067	0427	0428	0429	0429	0430	0431	0431	0432	0433	0433
0·068	0434	0434	0435	0436	0436	0437	0438	0438	0439	0440
0·069	0440	0441	0441	0442	0443	0443	0444	0445	0445	0446
0·070	0447	0447	0448	0449	0449	0450	0450	0451	0452	0452
0·071	0453	0454	0454	0455	0456	0456	0457	0457	0458	0459
0·072	0459	0460	0461	0461	0462	0463	0463	0464	0464	0465
0·073	0466	0466	0467	0468	0468	0469	0470	0470	0471	0471
0·074	0472	0473	0473	0474	0475	0475	0476	0477	0477	0478
0·075	0479	0479	0480	0481	0482	0482	0482	0483	0484	0484
0·076	0485	0486	0486	0487	0487	0488	0489	0489	0490	0491
0·077	0491	0492	0493	0493	0494	0494	0495	0496	0496	0497
0·078	0498	0498	0499	0500	0500	0501	0501	0502	0503	0503
0·079	0504	0505	0505	0506	0507	0507	0508	0508	0509	0510
0·080	0510	0511	0512	0512	0513	0514	0514	0515	0516	0516
0·081	0517	0517	0518	0519	0519	0520	0521	0521	0522	0523
0·082	0523	0524	0524	0525	0526	0526	0527	0528	0528	0529
0·083	0530	0530	0531	0531	0532	0533	0533	0534	0535	0535
0·084	0536	0537	0537	0538	0538	0539	0540	0540	0541	0542

Table XCI.—$Mg_2P_2O_7$ to P_2O_5.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. P_2O_5.									
	0	1	2	3	4	5	6	7	8	9
0·085	0542	0543	0544	0544	0545	0545	0546	0547	0547	0548
0·086	0549	0549	0550	0551	0551	0552	0553	0553	0554	0554
0·087	0555	0556	0556	0557	0558	0558	0559	0560	0560	0561
0·088	0561	0562	0563	0563	0564	0565	0565	0566	0567	0567
0·089	0568	0568	0569	0570	0570	0571	0572	0572	0573	0574
0·090	0574	0575	0575	0576	0577	0577	0578	0579	0579	0580
0·091	0581	0581	0582	0582	0583	0584	0584	0585	0586	0586
0·092	0587	0588	0588	0589	0590	0590	0591	0591	0592	0593
0·093	0593	0594	0595	0595	0596	0597	0597	0598	0598	0599
0·094	0600	0600	0601	0602	0602	0603	0603	0604	0605	0605
0·095	0606	0607	0607	0608	0609	0609	0610	0611	0611	0612
0·096	0612	0613	0614	0614	0615	0616	0616	0617	0618	0618
0·097	0619	0619	0620	0621	0621	0622	0623	0623	0624	0625
0·098	0625	0626	0627	0627	0628	0628	0629	0630	0630	0631
0·099	0632	0632	0633	0634	0634	0635	0635	0636	0637	0637
0·100	0638	0639	0639	0640	0641	0641	0642	0642	0643	0644
0·101	0644	0645	0646	0646	0647	0648	0649	0649	0650	0650
0·102	0651	0651	0652	0653	0654	0654	0655	0656	0656	0657
0·103	0657	0658	0658	0659	0660	0660	0661	0662	0662	0663
0·104	0664	0664	0665	0665	0666	0667	0667	0668	0669	0669
0·105	0670	0671	0671	0672	0672	0673	0674	0674	0675	0676
0·106	0676	0677	0678	0678	0679	0679	0680	0681	0681	0682
0·107	0683	0683	0684	0685	0685	0686	0686	0687	0688	0688
0·108	0689	0690	0690	0691	0692	0693	0693	0694	0694	0695
0·109	0695	0696	0697	0698	0698	0699	0699	0700	0701	0701
0·110	0702	0702	0703	0704	0704	0705	0706	0706	0707	0708
0·111	0708	0709	0709	0710	0711	0711	0712	0713	0713	0714
0·112	0715	0715	0716	0716	0717	0718	0718	0719	0720	0720
0·113	0721	0722	0722	0723	0723	0724	0725	0725	0726	0727
0·114	0727	0728	0729	0729	0730	0731	0731	0732	0732	0733
0·115	0734	0734	0735	0736	0736	0737	0738	0738	0739	0739
0·116	0740	0741	0741	0742	0743	0743	0744	0745	0745	0746
0·117	0746	0747	0748	0748	0749	0750	0750	0751	0752	0752
0·118	0753	0753	0754	0755	0755	0756	0757	0757	0758	0759
0·119	0759	0760	0760	0761	0762	0762	0763	0764	0764	0765
0·120	0766	0766	0767	0768	0769	0769	0770	0770	0771	0771
0·121	0772	0773	0773	0774	0775	0775	0776	0776	0777	0778
0·122	0778	0779	0780	0780	0781	0782	0782	0783	0783	0784
0·123	0785	0785	0786	0787	0787	0788	0789	0789	0790	0790
0·124	0791	0792	0792	0793	0794	0794	0795	0796	0796	0797
0·125	0798	0798	0799	0799	0800	0801	0801	0802	0803	0803
0·126	0804	0805	0805	0806	0806	0807	0808	0808	0809	0810
0·127	0810	0811	0812	0812	0813	0813	0814	0815	0815	0816
0·128	0817	0817	0818	0819	0819	0820	0820	0821	0822	0822
0·129	0823	0823	0824	0825	0825	0826	0827	0827	0828	0829

Table XCI.—$Mg_2P_2O_7$ to P_2O_5.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. P_2O_5.									
	0	1	2	3	4	5	6	7	8	9
0·130	0829	0830	0831	0831	0832	0833	0833	0834	0835	0835
0·131	0836	0836	0837	0838	0838	0839	0840	0840	0841	0842
0·132	0842	0843	0843	0844	0845	0845	0846	0847	0847	0848
0·133	0849	0849	0850	0850	0851	0852	0852	0853	0854	0854
0·134	0855	0856	0856	0857	0857	0858	0859	0859	0860	0860
0·135	0861	0862	0863	0863	0864	0864	0865	0866	0866	0867
0·136	0868	0868	0869	0870	0870	0871	0872	0872	0873	0873
0·137	0874	0875	0875	0876	0877	0877	0878	0879	0879	0880
0·138	0880	0881	0882	0882	0883	0884	0884	0885	0886	0886
0·139	0887	0887	0888	0889	0889	0890	0891	0891	0892	0893
0·140	0893	0894	0894	0895	0896	0896	0897	0898	0898	0899
0·141	0900	0900	0901	0901	0902	0903	0903	0904	0905	0905
0·142	0906	0907	0907	0908	0909	0909	0910	0910	0911	0912
0·143	0912	0913	0914	0914	0915	0916	0916	0917	0917	0918
0·144	0919	0919	0920	0921	0921	0922	0923	0923	0924	0924
0·145	0925	0926	0926	0927	0928	0928	0929	0930	0930	0931
0·146	0931	0932	0933	0933	0934	0935	0935	0936	0937	0937
0·147	0938	0938	0939	0940	0940	0941	0942	0942	0943	0944
0·148	0944	0945	0946	0946	0947	0947	0948	0949	0949	0950
0·149	0951	0951	0952	0953	0953	0954	0954	0955	0956	0956
0·150	0957	0957	0958	0959	0960	0960	0961	0961	0962	0963
0·151	0963	0964	0965	0965	0966	0967	0967	0968	0968	0969
0·152	0970	0970	0971	0972	0972	0973	0974	0974	0975	0976
0·153	0976	0977	0977	0978	0979	0979	0980	0981	0982	0982
0·154	0983	0983	0984	0984	0985	0986	0986	0987	0988	0988
0·155	0989	0990	0990	0991	0991	0992	0993	0993	0994	0995
0·156	0995	0996	0997	0997	0998	0998	0999	1000	1000	1001
0·157	1002	1002	1003	1004	1004	1005	1005	1006	1007	1007
0·158	1008	1009	1009	1010	1011	1011	1012	1013	1013	1014
0·159	1014	1015	1016	1016	1017	1018	1018	1019	1020	1020
0·160	1021	1021	1022	1023	1023	1024	1025	1025	1026	1027
0·161	1027	1028	1028	1029	1030	1030	1031	1032	1032	1033
0·162	1034	1034	1035	1035	1036	1037	1037	1038	1039	1039
0·163	1040	1041	1041	1042	1042	1043	1044	1044	1045	1046
0·164	1046	1047	1048	1048	1049	1050	1050	1051	1051	1052
0·165	1053	1053	1054	1055	1055	1056	1057	1057	1058	1058
0·166	1059	1060	1060	1061	1062	1062	1063	1064	1064	1065
0·167	1065	1066	1067	1067	1068	1069	1069	1070	1071	1071
0·168	1072	1072	1073	1074	1074	1075	1076	1076	1077	1078
0·169	1078	1079	1079	1080	1081	1081	1082	1083	1083	1084
0·170	1085	1085	1086	1087	1087	1088	1088	1089	1090	1090
0·171	1091	1092	1092	1093	1094	1094	1095	1095	1096	1097
0·172	1097	1098	1099	1099	1100	1101	1101	1102	1102	1103
0·173	1104	1104	1105	1106	1106	1107	1108	1108	1109	1109
0·174	1110	1111	1111	1112	1113	1113	1114	1115	1115	1116

Table XCI.—$Mg_2P_2O_7$ to P_2O_5.—*continued.*

Grm. $Mg_2P_2O_7$.	Grm. P_2O_5.									
	0	1	2	3	4	5	6	7	8	9
0·175	1117	1117	1118	1118	1119	1120	1120	1121	1122	1122
0·176	1123	1124	1124	1125	1125	1126	1127	1127	1128	1129
0·177	1129	1130	1131	1131	1132	1132	1133	1134	1134	1135
0·178	1136	1136	1137	1138	1138	1139	1139	1140	1141	1141
0·179	1142	1143	1143	1144	1145	1145	1146	1146	1147	1148
0·180	1148	1149	1150	1150	1151	1152	1152	1153	1154	1154
0·181	1155	1155	1156	1157	1157	1158	1159	1159	1160	1161
0·182	1161	1162	1162	1163	1164	1164	1165	1666	1166	1167
0·183	1168	1168	1169	1169	1170	1171	1171	1172	1173	1173
0·184	1174	1175	1175	1176	1176	1177	1178	1178	1179	1180
0·185	1180	1181	1182	1182	1183	1183	1184	1185	1185	1186
0·186	1187	1187	1188	1189	1189	1190	1191	1191	1192	1192
0·187	1193	1194	1194	1195	1195	1196	1197	1198	1198	1199
0·188	1199	1200	1201	1201	1202	1202	1203	1204	1205	1205
0·189	1206	1206	1207	1208	1208	1209	1210	1210	1211	1212
0·190	1212	1213	1213	1214	1215	1215	1216	1217	1217	1218
0·191	1219	1220	1220	1221	1221	1222	1223	1223	1224	1224
0·192	1225	1226	1226	1227	1228	1228	1229	1229	1230	1231
0·193	1231	1232	1233	1233	1234	1234	1235	1236	1236	1237
0·194	1238	1238	1239	1240	1240	1241	1241	1242	1243	1243
0·195	1244	1245	1245	1246	1247	1247	1248	1249	1249	1250
0·196	1250	1251	1252	1252	1253	1254	1254	1255	1256	1256
0·197	1257	1257	1258	1259	1259	1260	1261	1261	1262	1263
0·198	1263	1264	1264	1265	1266	1266	1267	1268	1268	1269
0·199	1270	1270	1271	1272	1272	1273	1273	1274	1275	1275

Table XCII.—Conversion of Grms. of Barium Sulphate into Grms. of Sulphur Trioxide.

(Factor 0·343.)

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·000	..	..	0001	0001	0001	0002	0002	0002	0003	0003
0·001	0003	0004	0004	0004	0005	0005	0005	0006	0006	0007
0·002	0007	0007	0008	0008	0008	0009	0009	0009	0010	0010
0·003	0010	0011	0011	0011	0012	0012	0012	0013	0013	0013
0·004	0014	0014	0014	0015	0015	0015	0016	0016	0016	0017
0·005	0017	0017	0018	0018	0019	0019	0019	0020	0020	0020
0·006	0021	0021	0021	0022	0022	0022	0023	0023	0023	0024
0·007	0024	0024	0025	0025	0026	0026	0026	0027	0027	0027
0·008	0028	0028	0028	0028	0029	0029	0029	0030	0030	0031
0·009	0031	0031	0032	0032	0032	0033	0033	0033	0034	0034
0·010	0034	0035	0035	0035	0036	0036	0036	0037	0037	0037
0·011	0038	0038	0038	0039	0039	0039	0040	0040	0040	0041
0·012	0041	0042	0042	0042	0043	0043	0043	0044	0044	0044
0·013	0045	0045	0045	0046	0046	0046	0047	0047	0047	0048
0·014	0048	0048	0049	0049	0049	0050	0050	0050	0051	0051
0·015	0051	0052	0052	0052	0053	0053	0054	0054	0054	0055
0·016	0055	0055	0056	0056	0056	0057	0057	0057	0058	0058
0·017	0058	0059	0059	0059	0060	0060	0060	0061	0061	0061
0·018	0062	0062	0062	0063	0063	0063	0064	0064	0064	0065
0·019	0065	0066	0066	0066	0067	0067	0067	0068	0068	0068
0·020	0069	0069	0069	0070	0070	0070	0071	0071	0071	0072
0·021	0072	0072	0073	0073	0073	0074	0074	0074	0075	0075
0·022	0075	0076	0076	0076	0077	0077	0078	0078	0078	0079
0·023	0079	0079	0080	0080	0080	0081	0081	0081	0082	0082
0·024	0082	0083	0083	0083	0084	0084	0084	0085	0085	0085
0·025	0086	0086	0086	0087	0087	0087	0088	0088	0088	0089
0·026	0089	0090	0090	0090	0091	0091	0091	0092	0092	0092
0·027	0093	0093	0093	0094	0094	0094	0095	0095	0095	0096
0·028	0096	0096	0097	0097	0097	0098	0098	0098	0099	0099
0·029	0099	0100	0100	0100	0101	0101	0102	0102	0102	0103
0·030	0103	0103	0104	0104	0104	0105	0105	0105	0106	0106
0·031	0106	0107	0107	0107	0108	0108	0108	0109	0109	0109
0·032	0110	0110	0110	0111	0111	0112	0112	0112	0113	0113
0·033	0113	0114	0114	0114	0115	0115	0115	0116	0116	0116
0·034	0117	0117	0117	0118	0118	0118	0119	0119	0119	0120
0·035	0120	0120	0121	0121	0121	0122	0122	0122	0123	0123
0·036	0123	0124	0124	0125	0125	0125	0126	0126	0126	0127
0·037	0127	0127	0128	0128	0128	0129	0129	0129	0130	0130
0·038	0130	0131	0131	0131	0132	0132	0132	0133	0133	0133
0·039	0134	0134	0134	0135	0135	0135	0136	0136	0136	0137

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·040	0137	0138	0138	0138	0139	0139	0139	0140	0140	0140
0·041	0141	0141	0141	0142	0142	0142	0143	0143	0143	0144
0·042	0144	0144	0145	0145	0145	0146	0146	0146	0147	0147
0·043	0147	0148	0148	0149	0149	0149	0150	0150	0150	0151
0·044	0151	0151	0152	0152	0152	0153	0153	0153	0154	0154
0·045	0154	0155	0155	0155	0156	0156	0156	0157	0157	0157
0·046	0158	0158	0158	0159	0159	0159	0160	0160	0161	0161
0·047	0161	0162	0162	0162	0163	0163	0163	0164	0164	0164
0·048	0165	0165	0165	0166	0166	0166	0167	0167	0167	0168
0·049	0168	0169	0169	0169	0169	0170	0170	0170	0171	0171
0·050	0172	0172	0172	0173	0173	0173	0174	0174	0174	0175
0·051	0175	0175	0176	0176	0176	0177	0177	0177	0178	0178
0·052	0178	0179	0179	0179	0180	0180	0180	0181	0181	0181
0·053	0182	0182	0182	0183	0183	0184	0184	0184	0185	0185
0·054	0185	0186	0186	0186	0187	0187	0187	0188	0188	0188
0·055	0189	0189	0189	0190	0190	0190	0191	0191	0191	0192
0·056	0192	0192	0193	0193	0193	0194	0194	0194	0195	0195
0·057	0196	0196	0196	0197	0197	0197	0198	0198	0198	0199
0·058	0199	0199	0200	0200	0200	0201	0201	0201	0202	0202
0·059	0202	0203	0203	0203	0204	0204	0204	0205	0205	0205
0·060	0206	0206	0206	0207	0207	0208	0208	0208	0209	0209
0·061	0209	0210	0210	0210	0211	0211	0211	0212	0212	0212
0·062	0213	0213	0213	0214	0214	0214	0215	0215	0215	0216
0·063	0216	0216	0217	0217	0218	0218	0218	0219	0219	0219
0·064	0220	0220	0220	0221	0221	0221	0222	0222	0222	0223
0·065	0223	0223	0224	0224	0224	0225	0225	0225	0226	0226
0·066	0226	0227	0227	0227	0228	0228	0228	0229	0229	0229
0·067	0230	0230	0230	0231	0231	0232	0232	0232	0233	0233
0·068	0233	0234	0234	0234	0235	0235	0235	0236	0236	0236
0·069	0237	0237	0237	0238	0238	0238	0239	0239	0239	0240
0·070	0240	0240	0241	0241	0241	0242	0242	0243	0243	0243
0·071	0244	0244	0244	0245	0245	0245	0246	0246	0246	0247
0·072	0247	0247	0248	0248	0248	0249	0249	0249	0250	0250
0·073	0250	0251	0251	0251	0252	0252	0252	0253	0253	0253
0·074	0254	0254	0255	0255	0255	0256	0256	0256	0257	0257
0·075	0257	0258	0258	0258	0259	0259	0259	0260	0260	0260
0·076	0261	0261	0261	0262	0262	0262	0263	0263	0263	0264
0·077	0264	0264	0265	0265	0265	0266	0266	0267	0267	0267
0·078	0268	0268	0268	0269	0269	0269	0270	0270	0270	0271
0·079	0271	0271	0272	0272	0272	0273	0273	0273	0274	0274
0·080	0274	0275	0275	0275	0276	0276	0276	0277	0277	0277
0·081	0278	0278	0279	0279	0279	0280	0280	0280	0281	0281
0·082	0281	0282	0282	0282	0283	0283	0283	0284	0284	0284
0·083	0285	0285	0285	0286	0286	0286	0287	0287	0287	0288
0·084	0288	0288	0289	0289	0289	0290	0290	0291	0291	0291

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·085	0292	0292	0292	0293	0293	0293	0294	0294	0294	0295
0·086	0295	0295	0296	0296	0296	0297	0297	0297	0298	0298
0·087	0298	0299	0299	0299	0300	0300	0300	0301	0301	0301
0·088	0302	0302	0303	0303	0303	0304	0304	0304	0305	0305
0·089	0305	0306	0306	0306	0307	0307	0307	0308	0308	0308
0·090	0309	0309	0309	0310	0310	0310	0311	0311	0311	0312
0·091	0312	0312	0313	0313	0314	0314	0314	0315	0315	0315
0·092	0316	0316	0316	0317	0317	0317	0318	0318	0318	0319
0·093	0319	0319	0320	0320	0320	0321	0321	0321	0322	0322
0·094	0322	0323	0323	0323	0324	0324	0324	0325	0325	0326
0·095	0326	0326	0327	0327	0327	0328	0328	0328	0329	0329
0·096	0329	0330	0330	0330	0331	0331	0331	0332	0332	0332
0·097	0333	0333	0333	0334	0334	0334	0335	0335	0335	0336
0·098	0336	0336	0337	0337	0338	0338	0338	0339	0339	0339
0·099	0340	0340	0340	0341	0341	0341	0342	0342	0342	0343
0·100	0343	0343	0344	0344	0344	0345	0345	0345	0346	0346
0·101	0346	0347	0347	0347	0348	0348	0348	0349	0349	0350
0·102	0350	0350	0351	0351	0351	0352	0352	0352	0353	0353
0·103	0353	0354	0354	0354	0355	0355	0355	0356	0356	0356
0·104	0357	0357	0357	0358	0358	0358	0359	0359	0359	0360
0·105	0360	0360	0361	0361	0362	0362	0362	0363	0363	0363
0·106	0364	0364	0364	0365	0365	0365	0366	0366	0366	0367
0·107	0367	0367	0368	0368	0368	0369	0369	0369	0370	0370
0·108	0370	0371	0371	0371	0372	0372	0372	0373	0373	0374
0·109	0374	0374	0375	0375	0375	0376	0376	0376	0377	0377
0·110	0377	0378	0378	0378	0379	0379	0379	0380	0380	0380
0·111	0381	0381	0381	0382	0382	0382	0383	0383	0383	0384
0·112	0384	0385	0385	0385	0386	0386	0386	0387	0387	0387
0·113	0388	0388	0388	0389	0389	0389	0390	0390	0390	0391
0·114	0391	0391	0392	0392	0392	0393	0393	0393	0394	0394
0·115	0394	0395	0395	0395	0396	0396	0397	0397	0398	0398
0·116	0398	0398	0399	0399	0399	0400	0400	0400	0401	0401
0·117	0401	0402	0402	0402	0403	0403	0403	0404	0404	0404
0·118	0405	0405	0405	0406	0406	0406	0407	0407	0407	0408
0·119	0408	0409	0409	0409	0410	0410	0410	0411	0411	0411
0·120	0412	0412	0412	0413	0413	0413	0414	0414	0414	0415
0·121	0415	0415	0416	0416	0416	0417	0417	0417	0418	0418
0·122	0418	0419	0419	0419	0420	0420	0421	0421	0421	0422
0·123	0422	0422	0423	0423	0423	0424	0424	0424	0425	0425
0·124	0425	0426	0426	0426	0427	0427	0427	0428	0428	0428
0·125	0429	0429	0429	0430	0430	0430	0431	0431	0431	0432
0·126	0432	0433	0433	0433	0434	0434	0434	0435	0435	0435
0·127	0436	0436	0436	0437	0437	0437	0438	0438	0438	0439
0·128	0439	0439	0440	0440	0440	0441	0441	0441	0442	0442
0·129	0442	0443	0443	0443	0444	0444	0445	0445	0445	0446

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·130	0446	0446	0447	0447	0447	0448	0448	0448	0449	0449
0·131	0449	0450	0450	0450	0451	0451	0451	0452	0452	0452
0·132	0453	0453	0453	0454	0454	0454	0455	0455	0456	0456
0·133	0456	0457	0457	0457	0458	0458	0458	0459	0459	0459
0·134	0460	0460	0460	0461	0461	0461	0462	0462	0462	0463
0·135	0463	0463	0464	0464	0464	0465	0465	0465	0466	0466
0·136	0466	0467	0467	0468	0468	0468	0469	0469	0469	0470
0·137	0470	0470	0471	0471	0471	0472	0472	0472	0473	0473
0·138	0473	0474	0474	0474	0475	0475	0475	0476	0476	0476
0·139	0477	0477	0477	0478	0478	0478	0479	0479	0480	0480
0·140	0480	0481	0481	0481	0482	0482	0482	0483	0483	0483
0·141	0484	0484	0484	0485	0485	0485	0486	0486	0486	0487
0·142	0487	0487	0488	0488	0488	0489	0489	0489	0490	0490
0·143	0490	0491	0491	0492	0492	0492	0493	0493	0493	0494
0·144	0494	0494	0495	0495	0495	0496	0496	0496	0497	0497
0·145	0497	0498	0498	0498	0499	0499	0499	0500	0500	0500
0·146	0501	0501	0501	0502	0502	0502	0503	0503	0504	0504
0·147	0504	0505	0505	0505	0506	0506	0506	0507	0507	0507
0·148	0508	0508	0508	0509	0509	0509	0510	0510	0510	0511
0·149	0511	0511	0512	0512	0512	0513	0513	0513	0514	0514
0·150	0515	0515	0515	0516	0516	0516	0517	0517	0517	0518
0·151	0518	0518	0519	0519	0519	0520	0520	0520	0521	0521
0·152	0521	0522	0522	0522	0523	0523	0523	0524	0524	0524
0·153	0525	0525	0525	0526	0526	0527	0527	0527	0528	0528
0·154	0528	0529	0529	0529	0530	0530	0530	0531	0531	0531
0·155	0532	0532	0532	0533	0533	0533	0534	0534	0534	0535
0·156	0535	0535	0536	0536	0536	0537	0537	0537	0538	0538
0·157	0539	0539	0539	0540	0540	0540	0541	0541	0541	0542
0·158	0542	0542	0543	0543	0543	0544	0544	0544	0545	0545
0·159	0546	0546	0546	0547	0547	0548	0548	0548	0549	0549
0·160	0549	0550	0550	0550	0551	0551	0551	0552	0552	0552
0·161	0553	0553	0553	0554	0554	0554	0555	0555	0555	0556
0·162	0556	0556	0557	0557	0557	0558	0558	0558	0559	0559
0·163	0559	0560	0560	0561	0561	0561	0562	0562	0562	0563
0·164	0563	0563	0564	0564	0564	0565	0565	0565	0566	0566
0·165	0566	0567	0567	0567	0568	0568	0568	0569	0569	0569
0·166	0570	0570	0570	0571	0571	0572	0572	0572	0573	0573
0·167	0573	0574	0574	0574	0575	0575	0575	0576	0576	0576
0·168	0577	0577	0577	0578	0578	0578	0579	0579	0579	0580
0·169	0580	0580	0581	0581	0581	0582	0582	0583	0583	0583
0·170	0584	0584	0584	0585	0585	0585	0586	0586	0586	0587
0·171	0587	0587	0588	0588	0588	0589	0589	0589	0590	0590
0·172	0590	0591	0591	0591	0592	0592	0592	0593	0593	0593
0·173	0594	0594	0595	0595	0595	0596	0596	0596	0597	0597
0·174	0597	0598	0598	0598	0599	0599	0599	0600	0600	0600

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·175	0601	0601	0601	0602	0602	0602	0603	0603	0603	0604
0·176	0604	0604	0605	0605	0605	0606	0606	0607	0607	0607
0·177	0608	0608	0608	0609	0609	0609	0610	0610	0610	0611
0·178	0611	0611	0612	0612	0612	0613	0613	0613	0614	0614
0·179	0614	0615	0615	0615	0616	0616	0616	0617	0617	0617
0·180	0618	0618	0619	0619	0619	0620	0620	0620	0621	0621
0·181	0621	0622	0622	0622	0623	0623	0623	0624	0624	0624
0·182	0625	0625	0625	0626	0626	0626	0627	0627	0627	0628
0·183	0628	0628	0629	0629	0629	0630	0630	0631	0631	0631
0·184	0632	0632	0632	0633	0633	0633	0634	0634	0634	0635
0·185	0635	0635	0636	0636	0636	0637	0637	0637	0638	0638
0·186	0638	0639	0639	0639	0640	0640	0640	0641	0641	0641
0·187	0642	0642	0643	0643	0643	0644	0644	0644	0645	0645
0·188	0645	0646	0646	0646	0647	0647	0647	0648	0648	0648
0·189	0649	0649	0649	0650	0650	0650	0651	0651	0651	0652
0·190	0652	0652	0653	0653	0654	0654	0654	0655	0655	0655
0·191	0656	0656	0656	0657	0657	0657	0658	0658	0658	0659
0·192	0659	0659	0660	0660	0660	0660	0661	0661	0661	0662
0·193	0662	0662	0663	0663	0663	0664	0664	0664	0665	0665
0·194	0665	0666	0666	0666	0667	0667	0667	0668	0668	0669
0·195	0669	0669	0670	0670	0670	0671	0671	0671	0672	0672
0·196	0672	0673	0673	0673	0674	0674	0674	0675	0675	0675
0·197	0676	0676	0676	0677	0677	0677	0678	0678	0678	0679
0·198	0679	0679	0680	0680	0681	0681	0681	0682	0682	0682
0·199	0683	0683	0683	0684	0684	0684	0684	0685	0685	0685
0·200	0686	0686	0686	0687	0687	0687	0688	0688	0688	0689
0·201	0689	0689	0690	0690	0690	0691	0691	0691	0692	0692
0·202	0692	0693	0693	0693	0694	0694	0695	0695	0695	0696
0·203	0696	0696	0697	0697	0697	0698	0698	0698	0699	0699
0·204	0699	0700	0700	0700	0701	0701	0701	0702	0702	0702
0·205	0703	0703	0703	0704	0704	0704	0705	0705	0705	0706
0·206	0706	0707	0707	0707	0708	0708	0708	0709	0709	0709
0·207	0710	0710	0710	0711	0711	0711	0712	0712	0712	0713
0·208	0713	0713	0714	0714	0714	0715	0715	0715	0716	0716
0·209	0716	0717	0717	0717	0718	0718	0719	0719	0719	0720
0·210	0720	0720	0721	0721	0721	0722	0722	0722	0723	0723
0·211	0723	0724	0724	0724	0725	0725	0725	0726	0726	0726
0·212	0727	0727	0727	0728	0728	0728	0729	0729	0730	0730
0·213	0730	0731	0731	0731	0732	0732	0732	0733	0733	0733
0·214	0734	0734	0734	0735	0735	0735	0736	0736	0736	0737
0·215	0737	0737	0738	0738	0738	0739	0739	0739	0740	0740
0·216	0740	0741	0741	0742	0742	0742	0743	0743	0743	0744
0·217	0744	0744	0745	0745	0745	0746	0746	0746	0747	0747
0·218	0747	0748	0748	0748	0749	0749	0749	0750	0750	0750
0·219	0751	0751	0751	0752	0752	0752	0753	0753	0754	0754

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·220	0754	0755	0755	0755	0756	0756	0756	0757	0757	0757
0·221	0758	0758	0758	0759	0759	0759	0760	0760	0760	0761
0·222	0761	0761	0762	0762	0762	0763	0763	0763	0764	0764
0·223	0764	0765	0765	0766	0766	0766	0767	0767	0767	0768
0·224	0768	0768	0769	0769	0769	0770	0770	0770	0771	0771
0·225	0771	0772	0772	0772	0773	0773	0773	0774	0774	0774
0·226	0775	0775	0775	0776	0776	0776	0777	0777	0778	0778
0·227	0778	0779	0779	0779	0780	0780	0780	0781	0781	0781
0·228	0782	0782	0782	0783	0783	0783	0784	0784	0784	0785
0·229	0785	0785	0786	0786	0786	0787	0787	0787	0788	0788
0·230	0788	0789	0789	0789	0790	0790	0790	0791	0791	0791
0·231	0792	0792	0792	0793	0793	0793	0794	0794	0794	0795
0·232	0795	0795	0796	0796	0796	0797	0797	0797	0798	0798
0·233	0798	0799	0799	0799	0800	0800	0800	0801	0801	0801
0·234	0802	0802	0802	0803	0803	0803	0804	0804	0804	0805
0·235	0805	0805	0806	0806	0806	0807	0807	0807	0808	0808
0·236	0808	0809	0809	0810	0810	0810	0811	0811	0811	0812
0·237	0812	0812	0813	0813	0813	0814	0814	0814	0815	0815
0·238	0815	0816	0816	0816	0817	0817	0817	0818	0818	0818
0·239	0819	0819	0819	0820	0820	0820	0821	0821	0822	0822
0·240	0822	0823	0823	0823	0824	0824	0824	0825	0825	0825
0·241	0826	0826	0826	0827	0827	0827	0828	0828	0828	0829
0·242	0829	0829	0830	0830	0830	0831	0831	0831	0832	0832
0·243	0832	0833	0833	0834	0834	0834	0835	0835	0835	0836
0·244	0836	0836	0837	0837	0837	0838	0838	0838	0839	0839
0·245	0839	0840	0840	0840	0841	0841	0841	0842	0842	0842
0·246	0843	0843	0843	0844	0844	0844	0845	0845	0846	0846
0·247	0846	0847	0847	0847	0848	0848	0848	0849	0849	0849
0·248	0850	0850	0850	0851	0851	0851	0852	0852	0853	0853
0·249	0853	0853	0854	0854	0854	0855	0855	0855	0856	0856
0·250	0857	0857	0857	0858	0858	0858	0859	0859	0859	0860
0·251	0860	0860	0861	0861	0861	0862	0862	0862	0863	0863
0·252	0863	0864	0864	0864	0865	0865	0865	0866	0866	0866
0·253	0867	0867	0867	0868	0868	0868	0869	0869	0869	0870
0·254	0870	0870	0871	0871	0871	0872	0872	0872	0873	0873
0 255	0874	0874	0874	0875	0875	0875	0876	0876	0876	0877
0·256	0877	0877	0878	0878	0878	0879	0879	0879	0880	0880
0·257	0881	0881	0881	0882	0882	0882	0883	0883	0883	0884
0·258	0884	0884	0885	0885	0885	0886	0886	0886	0887	0887
0·259	0887	0888	0888	0888	0889	0889	0889	0890	0890	0890
0·260	0891	0891	0891	0892	0892	0893	0893	0893	0894	0894
0·261	0894	0895	0895	0895	0896	0896	0896	0897	0897	0897
0·262	0898	0898	0898	0899	0899	0899	0900	0900	0900	0901
0·263	0901	0901	0902	0902	0902	0903	0903	0903	0904	0904
0·264	0905	0905	0905	0906	0906	0906	0907	0907	0907	0908

Table XCII.—$BaSO_4$ to SO_3.—*continued.*

Grm. $BaSO_4$.	Grm. SO_3.									
	0	1	2	3	4	5	6	7	8	9
0·265	0908	0908	0909	0909	0909	0910	0910	0910	0911	0911
0·266	0911	0912	0912	0912	0913	0913	0913	0914	0914	0914
0·267	0915	0915	0915	0916	0916	0917	0917	0917	0918	0918
0·268	0918	0919	0919	0919	0920	0920	0920	0921	0921	0921
0·269	0922	0922	0922	0923	0923	0923	0924	0924	0924	0925
0·270	0925	0925	0926	0926	0926	0927	0927	0928	0928	0928
0·271	0929	0929	0929	0930	0930	0930	0931	0931	0931	0932
0·272	0932	0932	0933	0933	0933	0934	0934	0934	0935	0935
0·273	0935	0936	0936	0936	0937	0937	0937	0938	0938	0938
0·274	0939	0939	0940	0940	0940	0941	0941	0941	0942	0942
0·275	0942	0943	0943	0943	0944	0944	0944	0945	0945	0945
0·276	0946	0946	0946	0947	0947	0947	0948	0948	0948	0949
0·277	0949	0949	0950	0950	0950	0951	0951	0952	0952	0952
0·278	0953	0953	0953	0954	0954	0954	0955	0955	0955	0956
0·279	0956	0956	0957	0957	0957	0958	0958	0958	0959	0959
0·280	0960	0960	0961	0961	0961	0962	0962	0962	0963	0963
0·281	0963	0964	0964	0964	0965	0965	0965	0966	0966	0966
0·282	0967	0967	0967	0968	0968	0968	0969	0969	0969	0970
0·283	0970	0970	0971	0971	0971	0972	0972	0972	0973	0973
0·284	0973	0974	0974	0974	0975	0975	0975	0976	0976	0977
0·285	0977	0977	0978	0978	0978	0979	0979	0979	0980	0980
0·286	0980	0981	0981	0981	0982	0982	0982	0983	0983	0983
0·287	0984	0984	0984	0985	0985	0985	0986	0986	0986	0987
0·288	0987	0987	0988	0988	0988	0989	0989	0990	0990	0990
0·289	0991	0991	0991	0992	0992	0992	0993	0993	0993	0994
0·290	0994	0994	0995	0995	0995	0996	0996	0997	0998	0998
0·291	0998	0999	0999	0999	1000	1000	1000	1001	1001	1001
0·292	1002	1002	1002	1003	1003	1003	1004	1004	1004	1005
0·293	1005	1005	1006	1006	1006	1007	1007	1007	1008	1008
0·294	1008	1009	1009	1009	1010	1010	1010	1011	1011	1012
0·295	1012	1012	1013	1013	1013	1014	1014	1014	1015	1015
0·296	1015	1016	1016	1016	1017	1017	1017	1018	1018	1018
0·297	1019	1019	1019	1020	1020	1020	1021	1021	1021	1022
0·298	1022	1022	1023	1023	1024	1024	1024	1025	1025	1025
0·299	1026	1026	1026	1027	1027	1027	1028	1028	1028	1029

Table XCIII.—Conversion of Grms. of Lead Sulphate into Grms. of Lead Monoxide.

(Factor 0·736.)

Grm. $PbSO_4$.	Grm. PbO.									
	0	1	2	3	4	5	6	7	8	9
0·00	..	0007	0015	0022	0029	0037	0044	0051	0059	0066
0·01	0073	0081	0088	0096	0103	0110	0118	0125	0132	0140
0·02	0147	0154	0162	0169	0177	0184	0191	0199	0206	0213
0·03	0221	0228	0235	0243	0250	0258	0265	0272	0280	0287
0·04	0294	0302	0309	0316	0324	0331	0339	0346	0353	0361
0·05	0368	0375	0383	0390	0397	0405	0412	0419	0427	0434
0·06	0442	0449	0456	0464	0471	0478	0486	0493	0500	0508
0·07	0515	0522	0530	0537	0544	0552	0559	0567	0574	0581
0·08	0589	0596	0603	0611	0618	0626	0633	0640	0648	0655
0·09	0662	0670	0677	0684	0692	0699	0706	0714	0721	0729
0·10	0736	0743	0751	0758	0765	0772	0780	0787	0795	0802
0·11	0810	0817	0824	0832	0839	0846	0854	0861	0868	0876
0·12	0883	0891	0898	0905	0913	0920	0927	0935	0942	0949
0·13	0957	0964	0971	0979	0986	0994	1001	1008	1016	1023
0·14	1030	1038	1045	1052	1060	1067	1074	1082	1089	1097
0·15	1104	1111	1119	1126	1133	1141	1148	1155	1163	1170
0·16	1178	1185	1192	1200	1207	1214	1222	1229	1236	1244
0·17	1251	1258	1266	1273	1281	1288	1295	1303	1310	1317
0·18	1324	1332	1339	1347	1354	1362	1369	1376	1384	1391
0·19	1398	1406	1413	1420	1428	1435	1442	1450	1457	1465
0·20	1472	1479	1487	1494	1501	1509	1516	1523	1531	1538
0·21	1546	1553	1560	1568	1575	1582	1590	1597	1604	1612
0·22	1619	1626	1634	1641	1649	1656	1663	1671	1678	1685
0·23	1693	1700	1707	1715	1722	1730	1737	1744	1752	1759
0·24	1766	1774	1781	1788	1796	1803	1810	1818	1825	1833
0·25	1840	1847	1855	1862	1869	1877	1884	1891	1899	1906
0·26	1914	1921	1928	1936	1943	1950	1958	1965	1972	1980
0·27	1987	1994	2002	2009	2017	2024	2031	2039	2046	2053
0·28	2061	2068	2075	2083	2090	2098	2105	2112	2120	2127
0·29	2134	2142	2149	2156	2164	2171	2178	2186	2193	2201
0·30	2208	2215	2223	2230	2237	2245	2252	2259	2267	2274
0·31	2282	2289	2296	2304	2311	2318	2326	2333	2340	2348
0·32	2355	2362	2370	2377	2385	2392	2399	2407	2414	2421
0·33	2429	2436	2443	2451	2458	2466	2473	2480	2488	2495
0·34	2502	2510	2517	2524	2532	2539	2546	2554	2561	2569
0·35	2576	2583	2591	2598	2605	2613	2620	2627	2635	2642
0·36	2650	2657	2664	2672	2679	2686	2694	2701	2708	2716
0·37	2723	2730	2738	2745	2753	2760	2767	2775	2782	2789
0·38	2797	2804	2811	2819	2826	2834	2841	2848	2856	2863
0·39	2870	2878	2885	2892	2900	2907	2914	2922	2929	2937

Table XCIII.—$PbSO_4$ to PbO.—*continued.*

Grm. $PbSO_4$.	Grm. PbO.									
	0	1	2	3	4	5	6	7	8	9
0·40	2944	2951	2959	2966	2973	2981	2988	2995	3002	3010
0·41	3017	3025	3032	3040	3047	3054	3062	3069	3076	3084
0·42	3091	3098	3106	3113	3121	3128	3135	3143	3150	3157
0·43	3165	3172	3179	3187	3194	3202	3209	3216	3224	3231
0·44	3238	3246	3253	3260	3268	3275	3282	3290	3297	3304
0·45	3312	3319	3327	3334	3341	3349	3356	3363	3371	3378
0·46	3386	3393	3400	3408	3415	3422	3430	3437	3444	3452
0·47	3459	3466	3474	3481	3489	3496	3503	3511	3518	3525
0·48	3533	3540	3547	3555	3562	3570	3577	3584	3592	3599
0·49	3606	3614	3621	3628	3635	3643	3650	3658	3665	3673
0·50	3680	3687	3695	3702	3709	3717	3724	3731	3739	3746
0·51	3754	3761	3768	3776	3783	3790	3798	3805	3812	3820
0·52	3827	3834	3842	3849	3857	3864	3871	3879	3886	3893
0·53	3901	3908	3915	3923	3930	3938	3945	3952	3960	3967
0·54	3974	3982	3989	3996	4004	4011	4018	4026	4033	4041
0·55	4048	4055	4062	4070	4077	4085	4092	4099	4107	4114
0·56	4122	4129	4136	4144	4151	4158	4166	4173	4180	4188
0·57	4195	4202	4210	4217	4225	4232	4239	4247	4254	4261
0·58	4269	4276	4283	4291	4298	4306	4313	4320	4328	4335
0·59	4342	4350	4357	4364	4372	4379	4386	4394	4401	4409
0·60	4416	4423	4431	4438	4445	4453	4460	4467	4475	4482
0·61	4490	4497	4504	4512	4519	4526	4534	4541	4548	4556
0·62	4563	4570	4578	4585	4593	4600	4607	4615	4622	4629
0·63	4637	4644	4651	4659	4666	4674	4681	4688	4696	4703
0·64	4710	4718	4725	4732	4740	4747	4754	4762	4769	4777
0·65	4784	4791	4799	4806	4813	4821	4828	4835	4843	4850
0·66	4858	4865	4872	4880	4887	4894	4902	4909	4916	4924
0·67	4931	4938	4946	4953	4961	4968	4975	4983	4990	4997
0·68	5005	5012	5019	5027	5034	5042	5049	5056	5064	5071
0·69	5078	5086	5093	5100	5108	5115	5122	5130	5137	5145
0·70	5152	5159	5167	5174	5181	5189	5196	5203	5211	5218
0·71	5226	5233	5240	5248	5255	5262	5270	5277	5284	5292
0·72	5299	5306	5314	5321	5329	5336	5343	5351	5358	5365
0·73	5373	5380	5387	5394	5402	5410	5417	5424	5432	5439
0·74	5446	5454	5461	5468	5476	5483	5490	5498	5505	5513
0·75	5520	5527	5535	5542	5549	5557	5564	5571	5579	5586
0·76	5594	5601	5608	5616	5623	5630	5638	5645	5652	5660
0·77	5667	5674	5682	5689	5697	5704	5711	5719	5726	5733
0·78	5741	5748	5755	5763	5770	5778	5785	5792	5800	5807
0·79	5814	5822	5829	5836	5844	5851	5858	5866	5873	5881
0·80	5888	5895	5903	5910	5917	5925	5932	5939	5947	5954
0·81	5962	5969	5976	5984	5991	5998	6006	6013	6020	6028
0·82	6035	6042	6050	6057	6065	6072	6079	6087	6094	6101
0·83	6109	6116	6123	6131	6138	6146	6153	6160	6168	6175
0·84	6182	6190	6197	6204	6212	6219	6226	6234	6241	6249
0·85	6256	6263	6271	6278	6285	6293	6300	6307	6314	6322
0·86	6330	6337	6344	6351	6359	6366	6373	6381	6388	6396
0·87	6403	6410	6418	6425	6433	6440	6447	6455	6462	6469
0·88	6477	6484	6491	6499	6506	6514	6521	6528	6536	6543
0·89	6550	6558	6565	6572	6580	6587	6594	6602	6609	6617

Table XCIII.—PbSO$_4$ to PbO.—*continued.*

Grm. PbSO$_4$.	Grm. PbO.									
	0	1	2	3	4	5	6	7	8	9
0·90	6624	6631	6639	6646	6653	6661	6668	6675	6683	6690
0·91	6698	6705	6712	6720	6727	6734	6742	6749	6756	6764
0·92	6771	6778	6786	6793	6801	6808	6815	6822	6830	6837
0·93	6845	6852	6859	6867	6874	6882	6889	6896	6903	6911
0·94	6918	6926	6933	6940	6948	6955	6962	6970	6977	6985
0·95	6992	6999	7007	7014	7021	7029	7036	7043	7051	7058
0·96	7066	7073	7080	7088	7095	7102	7110	7117	7124	7132
0·97	7139	7146	7154	7161	7168	7176	7183	7191	7198	7205
0·98	7213	7220	7227	7235	7242	7250	7257	7264	7272	7279
0·99	7286	7294	7301	7308	7316	7323	7330	7338	7345	7353
1·00	7360	7367	7374	7382	7389	7396	7404	7411	7418	7426
1·01	7434	7441	7448	7455	7462	7470	7477	7484	7492	7499
1·02	7507	7514	7522	7529	7536	7543	7551	7558	7566	7573
1·03	7581	7588	7595	7603	7610	7618	7625	7632	7640	7647
1·04	7654	7662	7669	7677	7684	7691	7698	7706	7713	7720
1·05	7728	7735	7742	7749	7757	7764	7771	7779	7786	7794
1·06	7802	7809	7816	7823	7831	7838	7846	7853	7860	7867
1·07	7875	7882	7890	7897	7905	7912	7919	7927	7934	7941
1·08	7949	7956	7964	7971	7979	7986	7993	8001	8008	8015
1·09	8022	8030	8038	8045	8052	8060	8067	8074	8082	8089
1·10	8096	8103	8111	8118	8126	8133	8140	8147	8155	8162
1·11	8170	8177	8184	8191	8199	8207	8214	8221	8228	8236
1·12	8243	8251	8258	8265	8272	8280	8287	8294	8302	8310
1·13	8317	8324	8331	8339	8347	8355	8362	8369	8376	8383
1·14	8390	8397	8405	8413	8420	8428	8435	8442	8450	8457
1·15	8464	8471	8479	8486	8493	8501	8508	8515	8523	8530
1·16	8538	8545	8552	8560	8567	8574	8582	8589	8596	8604
1·17	8611	8619	8626	8633	8640	8648	8655	8662	8670	8677
1·18	8685	8692	8699	8706	8714	8721	8729	8737	8744	8751
1·19	8758	8766	8773	8781	8788	8796	8803	8810	8818	8825
1·20	8832	8840	8847	8854	8861	8869	8876	8883	8891	8898
1·21	8906	8913	8920	8927	8935	8942	8950	8957	8964	8972
1·22	8979	8987	8994	9001	9009	9016	9023	9031	9038	9045
1·23	9053	9060	9067	9075	9082	9090	9097	9104	9111	9119
1·24	9126	9134	9141	9149	9156	9164	9171	9178	9186	9193
1·25	9200	9208	9215	9223	9230	9237	9244	9252	9259	9266
1·26	9274	9281	9288	9295	9303	9310	9318	9325	9332	9340
1·27	9347	9354	9361	9369	9376	9384	9391	9398	9406	9413
1·28	9421	9428	9435	9443	9450	9457	9465	9472	9480	9487
1·29	9494	9501	9509	9516	9524	9531	9538	9546	9553	9560
1·30	9568	9575	9583	9590	9598	9605	9612	9620	9627	9634
1·31	9642	9649	9657	9664	9671	9678	9686	9693	9700	9707
1·32	9715	9722	9730	9737	9744	9751	9759	9767	9774	9781
1·33	9789	9796	9803	9810	9818	9825	9833	9840	9847	9854
1·34	9862	9870	9877	9884	9892	9899	9906	9913	9920	9928
1·35	9936	9943	9950	9957	9965	9972	9980	9988	9995	1·0001

Table XCIV.—Solvents for Precipitates in Munroe's Crucible.

O. D. Swett, *Journ. Amer. Chem. Soc.*, 31. 928, 1909.

(Salts are applied in aqueous solution unless otherwise specified.)

1. Water.
2. Alcohol.
3. Carbon disulphide.
4. Sulphuric acid with nitric acid or nitrates.
5. Sulphuric acid, concentrated or fuming, with ammonium chloride.
6. Nitric acid.
7. Carbon dioxide in aqueous solution.
8. Acetic acid.
9. Oxalic acid.
10. Hydrochloric acid with ammonium chloride or oxalic acid.
11. Hydrofluoric acid.
12. Potassium hydroxide.
13. Sodium hydroxide.
14. Ammonium hydroxide.
15. Potassium sulphide.
16. Potassium sulphide, yellow.
17. Sodium sulphide.
18. Sodium sulphide, yellow.
19. Ammonium sulphide.
20. Ammonium sulphide, yellow.
21. Potassium bisulphite.
22. Sodium thiosulphate.
23. Ammonium sulphate.
24. Ammonium nitrate.
25. Sodium hydrogen phosphate.
26. Ammonium oxalate.
27. Ammonium acetate, alkaline.
28. Ammonium tartrate, alkaline.
29. Potassium carbonate.
30. Sodium carbonate.
31. Potassium chlorate.
32. Ammonium carbonate.
33. Potassium chloride.
34. Potassium iodide.
35. Sodium chloride.
36. Ammonium chloride.
37. Ammonium fluoride, dry.
38. Calcium chloride.
39. Magnesium chloride.
40. Potassium cyanide.
41. Ferrous sulphate.
42. Silver nitrate.
43. Lead acetate.
44. Mercuric nitrate.
45. Ferric acetate.

Solvents for Precipitates in Condition for Weighing.

(Numbers indicate correspondingly numbered solvents in the preceding list. Hyphens indicate successive treatments ; commas indicate alternative treatments. Abbreviations : *h* = hot, *c* = concentrated, *d* = dilute.)

Precipitates.	Solvents	Precipitates.	Solvents.
Aluminium oxide	12ch-1-10, 13ch-1-10	Barium chromate	6, 10
Ammonium arsenomolybdate.	14.	Barium silicofluoride	36
Ammonium chloride	1h.	Barium sulphate	4h, 5h
Ammonium magnesium arsenate.	6, 10.	Bismuth	6d
Ammonium phosphomolybdate.	1h, 12, 13, 25, 26, 29, 30, 36	Bismuth carbonate (basic).	6, 10
Ammonium chloroplatinate.	1h	Bismuth chromate (basic).	6
Antimony	6-1-10	Bismuth nitrate (basic).	6
Antimony pentasulphide.	14h	Bismuth oxide	10
Antimony tetroxide	10ch	Bismuth oxychloride	10c
Antimony trisulphide.	10c, 12d, 15, 19	Bismuth sulphide	6ch-1-3
Arsenious sulphide	12, 13, 15. 17, 21, 29, 30	Cadmium carbonate	6d, 14
Barium carbonate	7, 24, 36	Cadmium oxide	4, 5, 6, 10, 14
Barium carbonate, ignited.	1h, 6d	Cadmium sulphide	4dh, 6, 10
		Calcium carbonate	6d, 10d
		Calcium carbonate, ignited.	1h, 6d, 10d
		Calcium fluoride	4-1, 10c
		Calcium oxalate	6, 22

Table XCIV.—*continued.*

Precipitates.	Solvents.
Calcium sulphate	23dh
Chromium oxide	6ch+31dry+42 or 43, 31dry h+1, 42dry h+6
Cobalt	6
Cobalt hydroxide	23, 24, 36
Cobaltous sulphate	1h
Cobaltous sulphide	4c, 5, 8c, 10c
Cupric hydroxide	6, 10, 14
Cupric sulphide	6h, 40
Cuprous oxide	4
Cuprous sulphide	6
Cuprous thiocyanate.	4
Gold	4c
Gold sulphides	16, 40
Iron acetate (basic)	10
Iron arsenate	6, 10
Iron formate (basic)	10
Iron hydroxide	6d, 10d.
Iron oxide	10c
Iron phosphate	10, 45
Iron succinate (basic)	4, 5, 6, 10
Iron sulphide	4, 10
Lead arsenate	6
Lead carbonate	6d
Lead chloride	1h
Lead chromate	6, 12
Lead oxalate	6d
Lead oxide	6d
Lead phosphate	6
Lead sulphate	24, 27, 28, 10ch, 6ch, 22, 12h, 13h, 14h
Lead sulphide	6c, 10c
Magnesium oxide	4d, 6d, 10d
Magnesium phosphate.	6, 10
Magnesium pyroarsenate.	6, 10
Magnesium pyrophosphate.	6, 8, 10, 6ch, 10ch
Magnesium sulphate	1h
Manganese dioxide	5h+9
Manganese sesquioxide.	4+9, 4+41
Manganese sulphide	4d, 6d, 10d
Manganous pyrophosphate.	4ch, 5h, 6ch, 10ch
Manganous sulphate	1
Mercuric oxide	6, 10
Mercuric sulphide	15+12
Mercurous chloride	6ch-1
Mercurous chromate	6ch
Mercurous phosphate	6
Metastannic acid	10, 13
Nickel	6c
Nickel oxide	10
Nickelous hydroxide	10d, 14, 23, 24, 36
Nickelous subsulphide.	6
Nickelous sulphate	1h
Nickelous sulphide	6
Palladium iodide	14
Platinum sulphide	16, 18
Potassium chloride	1h
Potassium cobaltic nitrite.	1h
Potassium fluoborate	1, 2d
Potassium chloroplatinate.	1h, 12h
Potassium sulphate	1h
Silica	11, 12h, 13h, 29h, 30h, 37-ignition
Silver	6d
Silver chloride	14h
Silver cyanide	14, 40
Silver iodide	34c, 22, 40, 44ch
Silver phosphate	6, 14
Silver sulphide	6ch-1-3
Sodium carbonate	1h
Sodium chloride	1h
Sodium chloroplatinate.	1h, 2
Sodium sulphate	1h
Stannic acid	10-1
Stannic oxide	36dry-ignition, 10-1
Stannic phosphate	12
Stannic sulphide (hydrous).	10ch, 12, 15, 17
Stannous sulphide (hydrous).	10c
Strontium carbonate	7, 24, 36
Strontium sulphate	33c, 35c, 38c, 39c
Uranyl pyroarsenate	6
Uranyl pyrophosphate.	4, 6, 10
Zinc oxide	10dh
Zinc sulphide	4, 6, 10

THE LIBRARY.

THE following books will be found useful on the shelves of the library attached to the laboratory. There are numerous other excellent works of general interest which have not been included in this list.

MINERAL AND ROCK ANALYSIS.

W. F. HILLEBRAND, *The Analysis of Silicate and Carbonate Rocks*, Washington, 1910.

No analyst who has to deal with silicates, and certainly no writer on the subject, can fail to acknowledge his indebtedness to this American chemist. The book describes the methods used by the chemists of the U.S. Geological Survey. The first edition: *Some Principles and Methods of Rock Analysis*, Washington, 1900, has been the means of raising the standard of silicate analyses all round.

H. S. WASHINGTON, *Manual of the Chemical Analysis of Rocks*, New York, 1904.

This excellent American book is based on an earlier edition of Hillebrand's brochure, and it gives more elaborate details of manipulation and the precautions to be observed to secure accurate results by those not specially conversant with silicate analyses.

M. DITTRICH, *Anleitung zur Gesteinanalyse*, Leipzig, 1905.

This also is an excellent book from the German point of view, and it covers much the same ground as Washington's manual.

GENERAL ANALYSIS.

C. R. FRESENIUS, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1875–87.

This is one of the classics, for it has played an important part in modern analytical chemistry. Although the latest edition is over twenty years old, there are few analytical laboratories without their "Fresenius." This work has been translated into many European languages.

L. L. DE KONINCK, *Lehrbuch der qualitativen und quantitativen chemischen Analyse*, Berlin, 1904. In zwei Bänden.

This is a kind of modernised "Fresenius," and it is very useful when awkward separations are being planned. Several alternative processes are usually given. Analysts are indebted to the Belgian chemist for many new ideas.

A. CLASSEN, *Ausgewählte Methoden der analytischen Chemie*, Braunschweig, 1901–3. In zwei Bänden.

This large two-volume German book describes the analytical methods for all the elements. It can scarcely be said to supplant, but rather does it supplement "Fresenius." This is usually the second book consulted after "Fresenius" when a new separation has to be taken in hand.

L. E. RIVOT, *Docimasie. Traité d'Analyse des Substances Minérales*, Paris, 1886.

This five-volume French work is a small encyclopædia on the subject, and is accordingly a reference book—not so much used now as formerly.

A. Carnot, *Traité d'Analyse des Substances Minérales*, Paris, 1898. In four volumes.

The fourth volume of this bulky French work is not yet published. There are some good things in the three volumes which have appeared, although the great lapse of time between the first and later volumes has not tended to make the work attractive. It is a modernised "Rivot."

F. Peters, *Handbuch der analytischen Chemie*, Heidelberg, 1912.

This promises to be a comprehensive work of fourteen volumes, to be published in parts. A start has been made with the volume to be devoted to Antimony, Arsenic, and Tin. It will probably be many years before the work approaches completion, but once completed, it will be as useful as the celebrated "Gmelin" published by the same firm. The Germans alone appear to possess the great patience required to give the world a book such as is here contemplated.

A. Rüdisüle, *Nachweis, Bestimmung und Trennung der chemischen Elemente*, Bern, 1913.

This promises to be a comprehensive work in eleven volumes. Vol. I., devoted to Arsenic, Antimony, Tin, Tellurium, and Selenium, has been published. It seems as if the work will clash with "Peters" previously mentioned. Either or both works, when completed, will be indispensable for reference.

C. Friedheim, *Leitfaden für die quantitative chemische Analyse, unter Mitberücksichtigung von Massanalyse, Gasanalyse, und Elektrolyse*, Berlin, 1905.

This is the 1905 edition of the old classical *Leitfaden* of C. F. Rammelsberg (1845), and it describes many difficult separations not commonly found in other manuals.

P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 1904.

This German book contains many novel processes not found described in other textbooks, and, like the preceding volume, it is useful when devising a plan for an unfamiliar separation.

F. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 1911. In zwei Bänden.

This well-known German book is equally familiar in its American dress. It is one of the best modern books for advanced exercises, and it is a very useful book of reference. The two volumes deal with both qualitative and quantitative analysis.

G. Chesneau, *Principes Théoriques et Pratiques d'Analyse Minérale*, Paris, 1912.

This French book, occupying 641 pages, is a general treatise on quantitative inorganic analysis. It also contains some applications of physical chemistry to analysis very neatly expressed. There is no danger of the student's attention being distracted by references to authorities. The chapter on phosphorus is particularly good.

G. Lunge und E. Berl, *Chemisch-technische Untersuchungsmethoden*, Berlin, 1910. In vier Bänden.

Although it is generally considered that the day of comprehensive text-books is past, and that the specialist requires monographs written by experts in his own subject, this work may be regarded as a library of small monographs. Each subject is treated by a specialist in that particular theme. The cost appears high if the whole set be purchased, because the mineral chemist will find he has also bought monographs on subjects he never crosses, and conversely. An English translation is in course of publication.

T. B. Stillman, *Engineering Chemistry: A Manual of Quantitative Chemical Analysis for the use of Students, Chemists, and Engineers*, Easton, Pa., 1910.

This book treats of the analysis of coal, gases, metals, ores, water, oils, paints, and several commercial products.

A. Meurice, *Cours d'Analyse Quantitative*, Paris, 1908.

This French book of 829 pages is mainly devoted to the analysis of technical products. Chapter III., for instance, deals with Cements, Mortars, Limestones, Dolomites, etc.; and Chapter IV. with Refractory Products, Sands, and Clays. The succeeding chapters deal with minerals to be treated for copper, iron, cobalt, nickel, manganese, etc.

Qualitative Analysis.

C. R. Fresenius, *Anleitung zur qualitativen chemischen Analyse*, Braunschweig, 1895.

This book has been through nearly twenty editions since its first publication at Bonn in 1841, and it has also been translated into all the important European languages. It is still a standard of reference.

A. B. Prescott and O. C. Johnson, *Qualitative Chemical Analysis*, New York, 1910.

A detailed study of the reactions of the different elements, and the elaboration of schemes for the treatment of complex mixtures.

J. Stieglitz, *The Elements of Qualitative Chemical Analysis*, New York, 1911. Two vols.

This work is largely occupied with descriptions of the physical chemistry of qualitative analysis.

Volumetric Analysis.

H. Beckurts, *Die Methoden der Massanalyse*, Braunschweig, 1910.

This is the latest edition of C. F. Mohr's classical *Lehrbuch der chemisch-analytischen Titriermethoden* (1855), and it is very thorough. The Germans excel in books of reference of this kind.

A. Classen, *Theorie und Praxis der Massanalyse*, Leipzig, 1912.

The unique feature of this book is the theoretical discussions which precede the directions for manipulation. Classen was the editor of the 1888 edition of Mohr's *Lehrbuch.*

F. Sutton, *A Systematic Handbook of Volumetric Analysis*, London, 1911.

This volume has been through numerous editions since its publication in 1863, and it has proved a valuable work of reference when a volumetric process for a particular determination is sought.

E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 1910.

This book describes some applications of titanous chloride in volumetric analysis. The titanous chloride process for titrating ferric iron directly is described on p. 49.

Special Treatises and Monographs.

F. A. Gooch, *Methods in Chemical Analysis*, New York, 1912.

Analysts generally are under many obligations to Prof. Gooch for new apparatus, new methods, and for the revision and improvement of many of the older processes. It is a great convenience to have Gooch's papers, abridged by himself, collected into one volume.

W. Crookes, *Select Methods in Chemical Analysis* (*chiefly Inorganic*), London, 1905.

This book, compiled by the editor of the *Chemical News*, is strongest when consulted for the rarer elements.

A. H. Low, *Technical Methods of Ore Analysis*, New York, 1906.

This American book is useful when rapid technical processes are required. It specialises chiefly in evaluating ores.

H. Brearley and F. Ibbotson, *The Analysis of Steel-Works Materials*, London, 1902.

Although designed for metallurgical work, this book contains many useful hints on the separation of the different metals.

A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 1908.

Like Brearley and Ibbotson's book, this is also a useful book to consult for unfamiliar separations, and it is a most popular book of its kind.

H. Brearley, *The Analytical Chemistry of Uranium*, London, 1903.

Brearley's monograph reviews the analytical chemistry of uranium, and it is a pity that more monographs of a similar kind are not available for other metals.

R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erde und der Erdsäuren*, Stuttgart, 1902.

This monograph treats of the analysis of minerals containing the rare earths, thorium, zirconium, titanium, niobium, and tantalum.

L. Moser, *Die Bestimmungsmethoden des Wismuths*, Stuttgart, 1909.

The author has tried in this monograph to give as complete as possible a review of the analytical chemistry of bismuth.

H. Nissenson, *Die Untersuchungsmethoden des Zinks*, Stuttgart, 1907.

The author of this monograph has collected those methods employed for the determination of zinc, and more particularly those applicable to the technically important zinc ores.

L. Parry, *The Assay of Tin and Antimony*, London, 1906.

The writer of this monograph is mainly concerned with the methods for the separation and analytical determination of tin and antimony working under industrial conditions against time.

A. Stähler, *Handbuch der Arbeitsmethoden in der anorganischen Chemie*, Leipzig, 1913. Fünf Bände.

The first volume of this handbook deals with the mechanical operations, and the equipment of chemical laboratories. The other volumes have not yet appeared.

Electro-Analysis.

E. T. Smith, *Electro-analysis*, Philadelphia, 1907.

F. M. Perkin, *Practical Methods of Electrochemistry*, London, 1905.

A. Fischer, *Electroanalytische Schnellmethoden*, Stuttgart, 1908.

A. Hollard et L. Bertiaux, *Analyse des Métaux par Électrolyse*, Paris, 1909.

Cements.

F. R. von Arlt, *Laboratoriumsbuch für die Zementindustrie*, Halle a. S., 1910.

F. B. Gatehouse, *A Handbook for Cement Works Chemists*, London, 1908.

J. Malette, *Analyse Chimique des Chaux et Ciments*, Paris, 1911.

E. Leduc and G. Chenu, *Chaux, Ciments, Plâtres*, Paris, 1912.

R. K. Meade, *Portland Cement: Its Composition, Raw Materials, Manufacture, Testing, and Analysis*, Easton, Pa., 1906.

Assaying.

C. H. Fulton, *A Manual of Fire Assaying*, New York, 1907.

C. and J. J. Beringer, *A Text-book of Assaying*, London, 1908.

P. de P. Ricketts and E. H. Miller, *Notes on Assaying*, New York, 1908.

C. H. Aron, *Assaying*, San Francisco, 1900.

T. K. Rose, *The Metallurgy of Gold*, London, 1906.

Although the first eighteen chapters are concerned with the metallurgy of gold, the nineteenth and twentieth chapters are devoted to the assay of gold ores and bullion. Rose is an expert on this subject.

WATER.

W. P. Mason, *Examination of Water (Chemical and Bacteriological)*, New York, 1910.

H. B. Stocks, *Water Analysis for Sanitary and Technical Purposes*, London, 1912.

American Public Health Association, *Standard Methods for the Examination of Water and Sewage*, New York, 1912.

FUEL AND GAS.

E. E. Somermeier, *Coal: its Composition, Analysis, Utilisation, and Valuation*, New York, 1912.

J. H. Coste, *The Calorific Power of Gas: A Treatise on Calorific Standards and Calorimetry*, London, 1911.

J. S. Haldane, *Methods of Air Analysis*, London, 1912.

W. Hempel, *Gasanalytische Methode*, Braunschweig, 1900; English edition, 1902.

H. Franzen, *Gasanalytische Uebungen. Ein Hilfsbuch für das gasanalytische Praktikum*, Leipzig, 1907.

This booklet describes some exercises in the manipulation of gases. There is an English translation.

THEORETICAL.

W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Leipzig, 1910.

This is an extremely interesting book on the theory of analytical chemistry, and, when first published in 1894, it drew the serious attention of analysts to the significance and importance of the theory of their art. An English translation is available.

G. Chesneau, *Principes Théoriques des Méthodes d'Analyse Minérale, fondées sur les Réactions Chimiques*, Paris, 1906.

Like the preceding volume, this work treats of the theory, but whereas the former uses the language of the ionic hypothesis, Chesneau's book does not. An American translation is available.

PERIODICALS.

Zeitschrift für analytische Chemie. H. and W. Fresenius and E. Hintz, Wiesbaden; 18s. per ann.

The Analyst. Organ of the Society of Public Analysts, W. I. Sykes, London; 21s. per ann.

Annales de Chimie Analytique appliquée à l'Industrie, à la Pharmacie et à la Biologie, C. Crinon, Paris; 12s. per ann.

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